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THE

CHEMICAL GAZETTE,

OR,

JOURNAL OF PRACTICAL CHEMISTRY,

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS AND MANUFACTURES.

CONDUCTED BY

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Oxidation of Uric Acid by means of Potash and Ferridcyanide of Potassium. *By* A. SCHLIEPER.

ALTHOUGH a great many products of the decomposition of uric acid have been discovered during the last ten years, yet they were nearly all obtained only by the oxidating influence of acids or acid bodies. The oxidating action of brown oxide of lead and nitric acid on uric acid has been investigated by Liebig and Wöhler in a masterly manner*. I have already demonstrated the formation of a loxan and urea from uric acid, by the action of chlorate of potash and hydrochloric acid. With these exceptions, the influence of no other oxidating body on uric acid has ever been the subject of an original investigation. For these reasons it seemed to me interesting to study the oxidation of uric acid in an alkaline solution, because its decomposition, effected altogether by a new mode, might throw light on many points still enigmatical in the constitution of the products of the decomposition of uric acid.

A notice from Mercer, in regard to the bleaching of cotton cloth dyed indigo-blue by means of a solution of caustic potash and ferridcyanide of potassium, suggested to me the idea of applying the same mode of oxidation to uric acid; but in doing so I found it exceedingly difficult to separate the resulting salts of potash in such a way that the newly-generated and so easily decomposable products of uric acid should remain unchanged.

It is well known that 1 equiv. of ferridcyanide of potassium with 1 equiv. of potash are decomposed in presence of oxidizable substances, in such a manner that the red prussiate of potash takes up 1 equiv. of potassium, forming with it 2 equivs. of ferrocyanide of potassium, during which the oxygen of the potash set free combines with the oxidizable body.

Ferridcyanide of potassium $3KCy + Fe^2 Cy^3 = 3KCy + Fe^2 Cy^2 + Cy$ with potash $(K + O) = 2$ equivs. of prussiate of potash $= 4KCy + Fe^2 Cy^2$, and 1 equiv. of oxygen.

* Ann. der Chem. und Pharm., vol. xxvi. p. 241.

I communicate the following results as they presented themselves in the course of the investigation.

To observe the action of ferridcyanide of potassium and potash on uric acid, some previous experiments were made, in which very small quantities of powdered red prussiate of potash were put into a nearly cold solution of uric acid in a little more potash ley than was necessary for the formation of neutral urate of potash, $2KO, C^{10} N^4 H^4 O^6$. The salt dissolves easily in the liquid, and is then directly changed into prussiate of potash. After the first additions of red prussiate of potash, a separation occurred of a thick reddish-white precipitate, by which the entire liquid was soon thickened to a pulp, which on closer investigation was found to consist of biurate of potash, $KO, C^{10} N^4 H^4 O^6$. So much potash and red prussiate of potash were alternately added, that the uric acid remained in permanent solution. As soon as biurate of potash separated, or as soon as the red prussiate of potash was not decomposed with facility, the addition of a few drops of solution of potash were sufficient to renew the operation. The addition of red prussiate of potash was continued till by a few drops of muriatic acid no uric acid was precipitated. Towards the end of the operation the decomposition of the uric acid proceeds slowly, and therefore the addition of red prussiate of potash must be made at greater intervals.

The alkaline liquor, which smells slightly of ammonia, and contains prussiate of potash, an excess of potash and the products of decomposition of uric acid, was then nearly neutralized with sulphuric acid; a considerable quantity of carbonic acid was disengaged, and the solution was evaporated by boiling; a constant smell of ammonia seemed to indicate a further decomposition of the generated organic bodies. The solution must not be perfectly neutralized with sulphuric acid, because then the prussiate of potash is decomposed during the evaporation, prussic acid goes off, and a white pulverulent combination, $KFe^2 Cy^3$, precipitates itself, which it is nearly impossible to separate, because it goes through every filter.

The greater part of the prussiate of potash was separated by crystallization; the mother-liquor was then evaporated to a small volume and mixed with alcohol, by which sulphate and prussiate of potash were precipitated; this precipitate was then boiled several times with alcohol to remove all substances soluble in the same. The alcoholic solution during evaporation gave crystalline crusts of an organic body, which were separated; the liquor was then concentrated to a syrup, but after long standing indicated traces only of indistinct crystals containing potash. This syrupy mass was soluble in a great quantity of *weak*, and could be again precipitated in thick white flakes by *absolute alcohol*. The residuary saline mass extracted with alcohol consisted mostly of prussiate and sulphate of potash, to which no attention was paid. Other processes were followed to detect the organic substances insoluble in alcohol, which were possibly present.

A second portion of uric acid was treated as the first, except that the solution, which contained principally free potash, carbonate and

prussiate of potash, and the organic bodies sought for, was now neutralized with acetic acid with the precautions before mentioned. On evaporating, a quantity of acetate of ammonia was evolved. After the greater part of the prussiate of potash had crystallized, the separated mother-liquor was precipitated by alcohol, and the precipitate exhausted several times with alcohol. A previous essay to separate the prussiate of potash by means of acetate of copper, and an excess of the latter by sulphuretted hydrogen, did not furnish a favourable result, because complex decompositions took place, and sulphur entered into the composition of the organic bodies. The evaporated alcoholic solution, which naturally contained a great quantity of acetate of potash, did not furnish a trace of crystals, but only the above-mentioned viscid syrup, which was separated from the acetate of potash by treating with absolute alcohol; this seemed to indicate that the first had sustained a further decomposition by boiling with acetate of potash, which conducts itself in many cases as a feeble alkali; the unmistakeable development of acetate of ammonia furnished the proof of such decomposition.

The residuary salts, insoluble in alcohol, were then dissolved in water, and the prussiate of potash precipitated from the hot solution by a very slight excess of acetate of copper; the filtered solution contained however neither prussiate of potash nor copper salts, a proof that the small excess of acetate of copper was precipitated by the organic matter present. This filtrate, treated with strong alcohol, afforded an abundant crystalline white precipitate, soluble in water, and crystallizing in well-formed crystals, which on further investigation proved to be *neutral oxalate of potash*. The presence of oxalic acid was further determined by the preparation and analysis of a salt of lead, which furnished 75·16 oxide of lead.

The purification of the previously-mentioned crystalline substance was effected very easily by crystallization of the watery solution, for this substance is difficultly soluble in cold, but easily soluble in hot water, and crystallizes on cooling in small transparent shining prisms; they have a neutral reaction, are easily soluble in alkalies, and develope ammonia when the alkaline solution is heated. After neutralizing with acetic acid and addition of muriate of lime, an abundant precipitate of oxalate of lime is formed. A solution of the same body, mixed with a small quantity of ammonia, gives a white precipitate with nitrate of silver. All these reactions pointed out *allantoin*, whose presence was perfectly confirmed by analysis.

The air-dried crystals furnished on combustion with chromate of lead—

			H=1.		
Carbon	29·91	30·13	4	= 24	30·37
Hydrogen	3·97	4·12	3	3	3·79
Nitrogen	35·17	..	2	28	35·18
Oxygen	..	..	3	24	30·66

The formation of ammonia and oxalic acid on heating and evaporating an alkaline allantoic solution were now explained; for allan-

toin is decomposed perfectly into these two products by boiling with alkalies:—$C^4 N^2 H^3 O^3 + 3HO = 2$ equivs. $NH^3 \times 2$ equivs. $C^2 O^3$.

I have mentioned before that the alcoholic solution, filtered from the allantoin, leaves by further evaporation a viscid syrup containing potash, which, though easily soluble in water, can be separated by an addition of absolute or strong alcohol to the watery solution, as a thick white flocculent precipitate. This precipitate, collected on a filter, absorbs moisture with great avidity and deliquesces; as such it is not fit for analysis; I therefore tried to combine the organic body with oxide of lead, and to analyse it as a lead salt. The watery solution of this substance was for this purpose mixed with a solution of neutral acetate of lead, by which a sparsing white precipitate was produced, consisting for the greatest part of oxalate of lead, which was filtered off. The liquid was then mixed in two portions with pure ammonia, free from carbonic acid, by which a white, thick, curdy precipitate was formed; only the first precipitation was used for the entire analysis. Dried, this lead salt appeared as a white shining powder, insoluble in cold water and alcohol, little soluble in hot water, easily soluble in acetic acid, and precipitable again by adding ammonia to this solution.

The amount of oxide of lead was determined from the first and second precipitation, and it varied from 67 to 73 per cent., as probably this mode of precipitation occasioned the formation of basic salts; on which account I was obliged to renounce the determination of the atomic weight of this body.

For the analysis, the lead salt was dried at 212° F.

I. 0·3127 grm. substance gave 0·2855 grm. sulphate of lead = 0·2100223 grm. oxide of lead = 67·16 PbO.

II. 0·3455 grm. substance gave 0·3165 grm. sulphate of lead = 0·2328269 grm. oxide of lead = 67·38 PbO.

III. 1·0433 grm. substance furnished on combustion with chromate of lead 0·3935 grm. carbonic acid and 0·1103 grm. water.

IV. 0·949 grm. substance furnished on combustion with chromate of lead 0·3568 grm. carbonic acid and 0·10 grm. water.

V. 0·683 grm. substance furnished on combustion with soda-lime, 0·8512 grm. platino-chloride of ammonium = 0·05345 grm. nitrogen.

In this case the relation of the atoms of oxide of lead and carbon is 6 : 17, which proves clearly that the determination of the lead in this salt is not decisive for establishing its atomic weight. If the mean amount of oxide of lead, 67·27, is subtracted, the following figures will express the composition of the combined organic body:—

	I.	II.
Carbon	10·28	10·25
Nitrogen	7·82	7·82
Hydrogen	1·18	1·15
Oxygen	19·22	19·15

From these values the following formula may be deduced, showing

exactly the composition of the organic substance in combination with the oxide of lead :—

$$C^6\,N^2\,H^4\,O^6.$$

The results of the comparison of the found and calculated values expressed in per-cents. is as follows :—

	Calculated.		Found.	
			I.	II.
C^6	36	31·03	31·40	31·31
N^2	28	24·13	23·89	23·89
H^4	4	3·44	3·60	3·51
O^6	48	41·40	41·11	41·29
	116	100·00	100·00	100·00

This body is a new acid, for which I propose the name of *lantanuric acid*. I shall have an opportunity, in the course of this paper, to return to this subject.

After the presence of allantoin was proved by analysis, it was clear that in the adopted way it was impossible to study the process of oxidation of uric acid here occurring, because the action of a hot alkaline solution on the generated products so easily occasions secondary decompositions. Hence I adopted a new mode for the decomposition of uric acid, and carefully avoided everything which could possibly occasion a decomposition of the newly-generated allantoin.

The solution of uric acid in potash ley was obtained as before; and to this an alkaline solution of 5 oz. uric acid in 1 gallon of water at 68° F. was added alternately for some time; also ferridcyanide of potassium and potash ley, till all uric acid was completely decomposed; to effect this there were necessary $20\frac{1}{2}$ oz. red prussiate of potash and $10\frac{1}{4}$ oz. hydrate of potash, which, expressed in equivalents, is nearly exactly :—

1 equiv. of uric acid, $C^{10}\,N^4\,H^4\,O^6$.
2 equivs. of ferridcyanide of potassium.
6 equivs. of hydrate of potash.

According to this only 2 equivs. of oxygen combine with 1 equiv. of uric acid. The alkaline solution was mixed with pure nitric acid nearly to neutralization; a great quantity of carbonic acid was disengaged, although the hydrate of potash originally employed in this experiment was freshly made and nearly free from carbonic acid, and as far as possible I had prevented the absorption of carbonic acid from the air. The solution became turbid and coloured soon after the neutralization (the same takes place when, instead of *nitric* acid, carbonic acid is used for the neutralization of the free alkali); and after a short time a small quantity of a light, flocculent, dirty brick-coloured precipitate separated, and nearly at the same time crystals of allantoin began to form in the liquid. The perfect separation of this red flocculent precipitate took place after three or four days, and the liquid then assumed the ordinary yellow colour of a con-

centrated solution of prussiate of potash; the crystallization of the allantoin required 8 to 10 days.

After the separation of allantoin and the red body by filtration, the filtered liquor was mixed with nitric acid till it exhibited a strong acid reaction, and then all prussiate of potash was precipitated by a solution of nitrate of lead, the prussiate of lead being insoluble in very dilute nitric acid, while the precipitation of an organic lead salt was thus perfectly prevented. After the separation of the prussiate of lead and the precipitation of a small excess of oxide of lead by means of sulphate of potash, the solution was perfectly neutralized with potash; after which operation it could only contain nitrate of potash and the problematic organic substances. Oxalic acid was not present. The nitrate of potash was separated for the greatest part, including a small portion of allantoin still present, by evaporation and crystallization. The mother-liquor, concentrated to a small volume, was then mixed with cold absolute alcohol, by means of which the greatest part of the nitrate of potash still present was precipitated with a small portion of the before-mentioned viscid body (lantanurate of potash). The filtered alcoholic solution was then evaporated to dryness in the water-bath. The very small crystalline residue was dissolved in water and mixed with concentrated nitric acid, when crystals of *nitrate of urea*, of the characteristic form, instantly separated; the whole amount of it did not exceed 2 to 3 grms. The identity of the nitrate of urea ($C^2 N^3 H^5 O^8$) was rendered unquestionable by combustion with oxide of copper.

This substance furnished in five tubes a relation of carbonic acid and nitrogen as 2:3, or together as 42,2 cub. cent. CO^2:66, 1 cub. c. N.

The quantity of the urea present is too small to allow of the idea that it proceeded from the direct oxidation of the uric acid. I consider it to be a secondary product of the decomposition of a small portion of allantoin; I shall show hereafter that the latter suffers an alteration in an alkaline solution; 2 equivs. of allantoin take into their composition 2 equivs. of water, and form an easily decomposable new acid, $C^8 N^4 H^8 O^8$; this acid separates most probably into urea and lantanuric acid by longer contact or heating with alkalies:—

$$C^8 N^4 H^8 O^8 \begin{cases} C^6 N^2 H^4 O^6 = \text{lantanuric acid.} \\ C^2 N^2 H^4 O^2 = \text{urea.} \end{cases}$$

The above-mentioned red flocculent body appears likewise in too inconsiderable a quantity to be deemed other than a secondary product of this new method of decomposing uric acid; the only products which appear in notable quantity are allantoin and carbonic acid. I have mentioned before that 2 equivs. of ferridcyanide of potassium were necessary to effect the decomposition of 1 equiv. of uric acid; thus 1 equiv. of uric acid has taken up 2 equivs. of oxygen; it now requires only 2 equivs. of water in addition, to allow of its separation into 2 equivs. of allantoin and 2 equivs. of carbonic acid. This simple decomposition of uric acid actually takes place in this process of oxidation. 1 equiv. uric acid + 2 equivs. ferridcyanide of potassium + 4 equivs. potash + 2 equivs. water form 4

equivs. of prussiate of potash, 2 equivs. of carbonate of potash and 2 equivs. of allantoin:—

1 eq. uric acid	$= C^{10}N^4H^4O^6$		2 eqs. allantoin, $C^8N^4H^6O^6$
2 eqs. oxygen	$= O^2$	$=$	2 eqs. carb. acid, C^2O^4
2 eqs. water	$= H^2O^2$		
	$C^{10}N^4H^6O^{10}$		$C^{10}N^4H^6O^{10}$

The excess of potash served on the one hand to hold in solution the resulting allantoin, and on the other to accelerate the decomposition.

I have not submitted the above-mentioned red flocculent substance to further investigation, because its quantity was very small, and I did not succeed in separating it perfectly from prussiate of potash and allantoin; the reactions made with it show, nevertheless, that it is a new and certainly an interesting body. It has nearly the same solubility in cold and hot water and alcohol as allantoin, and it could be obtained only in small quantity, washing the latter and filtering off. This red substance gives to water and alcohol a rich orange colour; is easily soluble in hot water, by which means the colour changes however to light yellow, and in cooling the watery solution deposits a fine sulphur-yellow precipitate; a great part remains however in solution. In potash and ammonia this red body is soluble with an orange colour; but after the addition of an acid, only a small portion of it separates with a light yellow colour. In boiling the alkaline solution, ammonia is formed, and acids added to the nearly colourless solution cause no further precipitate.

The quantity of the crystallized allantoin is very great; so that if an easy mode of separating the red body adhering so obstinately to it should be found out, this process would furnish perhaps the most advantageous mode of preparing it.

I succeeded, after many essays, by the following plan, but with great loss, in obtaining allantoin in perfect purity. Relying on the statement of Liebig and Wöhler, that cold potash ley did not exert any decomposing action on allantoin, the brick-coloured allantoin separated by means of water, as well as possible, from the prussiate of potash, was dissolved in concentrated cold potash ley, which was very easily effected; after filtration the orange-coloured alkaline liquor was directly mixed with acetic acid till the reaction became acid; a slight yellow turbidness resulted, occasioned by the red body, and soon afterwards allantoin began to deposit itself in small, nearly white crystals. By often repeated crystallization from hot water it was obtained perfectly pure, in white, shining, transparent, prismatic crystals.

By this mode of purifying allantoin, a great part of it remains behind in the solution of acetate of potash, which cannot be obtained by evaporation; on the contrary, a great quantity of acetate of ammonia goes off, indicating a new decomposition. The solution in acetate of potash, filtered from allantoin, was concentrated to a syrup in the water-bath, and then mixed with a considerable volume of

absolute alcohol, by which a thick, flocculent, nearly white precipitate of an organic potash compound resulted. The alcoholic solution was filtered from it, and evaporated to dryness; the residue consisted chiefly of acetate of potash, scarcely mixed with other organic substance; oxalic acid and urea were not found. The flocculent substance precipitated by alcohol was dissolved in a small quantity of water; only a few drops were sufficient to convert it into a syrup. From all reactions it seemed to be perfectly identical with the above-mentioned impure lantanurate of potash. The solution had an acid reaction, and afforded with acetate of lead an abundant white precipitate, in every respect like the lantanurate of lead already described. This solution ought to contain neutral or acid lantanurate of potash; hence the following plan was adopted to obtain one of these potash combinations fit for analysis. The syrup-like watery solution was very cautiously mixed with alcohol till a slight turbidness occurred, indicating the precipitation of the potash salt. The weak alcoholic solution was then left to itself; after a long time, crystals and crystalline crusts began to separate; from time to time a fresh quantity of alcohol was added, by which a new impulse was given to the crystallization. Finally, the crystallization terminated, when the liquid gradually lost its acid reaction and became neutral.

The separated crystals were *bilantanurate of potash*, as will be seen by the result of the following analysis. They were purified by repeated crystallization from water; and the attached yellow colouring matter became gradually insoluble, and could be separated by filtration.

The pure bilantanurate of potash crystallizes from the watery solution in hard crystalline crusts, which consist of an aggregation of very strong, shining, white, tabular crystals; it is soluble in 8 to 10 parts of cold, and in much less hot water, but it very slowly crystallizes out of the hot saturated solution when cooled; it is insoluble in strong alcohol. I added a small quantity of alcohol to the watery solution, and it directly became milky; but after a short time it cleared again, and the bilantanurate of potash deposited itself in small, dazzling, white, voluminous, acicular crystals. The solution of this salt gives with acetate of lead no precipitate; but after addition of alcohol a thick perfectly white precipitate results, which disappears again after the addition of more water; probably it is bilantanurate of lead, which is consequently easily soluble in water and insoluble in alcohol; there also results a thick, white, flocculent precipitate of lantanurate of lead if ammonia is added to a mixture of bilantanurate of potash and acetate of lead, or if the former is precipitated with basic acetate of lead. With nitrate of silver, on the addition of ammonia, a thick white precipitate of lantanurate of silver results, which is not changed by boiling. If bilantanurate of potash is neutralized with potash and evaporated, the solution dries without any signs of crystallization to a viscid syrup, precipitable by alcohol in flocks; the acid potash salt could not be reobtained in crystals by the addition of stronger acids. The thick mother-liquor filtered from

the impure bilantanurate of potash seemed to consist principally of the neutral potash salt, mixed with a small portion of another substance, which could be separated by acetate of lead as a white precipitate insoluble in acetic acid.

The salt employed for analysis was perfectly pure, and crystallized in small, dazzling, rhombic plates. It furnished—

Carbon	22·65	12 =	72	22·20
Hydrogen	4·09	13	13	4·01
Nitrogen	17·47	4	56	17·47
Oxygen	41·57	17	136	41·97
Potash	14·22	1	47·2	14·55

At 212° the salt lost 11·15 per cent. water; 4 equivs. require 11·10; the formula of this salt is therefore

$$KO, C^6 N^2 H^4 O^6 + HO, C^6 N^2 H^4 O^6 + 4aq.$$

The composition of lantanuric acid is $C^6 N^2 H^4 O^6 + HO$. The anhydrous acid may be considered as consisting of $2Cy + C^2 HO^3 + 3HO$, or as urea + 4 equivs. of carbonic oxide; it contains 1 equiv. of oxygen more than murexan and difluan.

Its formation from allantoin is very simple; the latter takes up 2HO in contact with alkalies, as already mentioned, and forms the new acid $C^8 N^4 H^8 O^8$, which divides itself on further contact with alkalies into urea and lantanuric acid. I mentioned that on examining the solution which was filtered from the allantoin, and consisted principally of prussiate of potash, lantanuric acid and urea were detected.

I have tried to separate the lantanuric acid from the lead salt by means of sulphuretted hydrogen. It forms an acid solution, which dries to a gum-like mass, uncrystallizable in water and alcohol. The quantity was however too small to allow me to make further experiments with it. Further, I have prepared the silver salt from the potash salt by neutralization with ammonia and separation by nitrate of silver, which caused a thick white precipitate. The lantanurate of silver was dried at 212° F., and was just sufficient for a determination of its atomic weight.

0·2645 grm. salt gave 0·140 grm. silver = 0·15097 grm. oxide of silver. Hence the atomic weight of this combination as calculated = 204. The atomic weight of the organic substance combined with silver consequently = 88. Expressed by a formula, the composition of this silver salt is—

$$AgO, C^6 N^2 HO^3.$$

Calculated in per cents.—

	Calculated.		Found.
1 equiv. AgO	116	56·61	56·84
1 .. $C^6 N^2 HO^3$	89	43·39	

Thus by drying the lantanurate of silver at 212° F., 3 equivs. of water are removed from antanuric acid. From the composition of the bilantanurate of potash and of the lantanurate of lead dried at 212°, it is however probable that in the analysed silver salt

the lantanuric acid was not present as such; nevertheless the composition of lantanuric acid must be expressed by the formula $C^6 N^2 H^4 O^6$, HO.

I had not enough of the substance to permit an analysis of the lantanurate of silver in an air-dried state, or to ascertain whether bilantanurate of potash would still give off water at a higher temperature without any change in its properties.

If a strong acid is directly added to pure allantoin dissolved in cold concentrated potash ley, nearly the whole of this substance precipitates if the alkaline liquor stands a long time. The quantity of allantoin precipitated becomes smaller and smaller, and after one or two days (in summer) all the allantoin is changed, and acids no longer precipitate that substance. If the solution is now boiled, only a small quantity of ammonia is evolved, and no oxalic acid is formed; hence no allantoin is present. If the colourless alkaline liquor is treated with acetic acid till an acid reaction is produced, and then alcohol added, the liquid becomes milky and clears again very soon, because the potash combination of the newly-formed acid separates at the bottom of the vessel as a concentrated, clear, oily liquid. All attempts to obtain the potash salt in a crystalline form failed; mixed with water, it gives an abundant white precipitate with nitrate of silver, becoming black on boiling. To estimate the composition of this new acid, to which may be given the name hydallantoinic acid, I used a lead salt. Allantoin was dissolved in cold concentrated potash ley; after two days' standing acetic acid was added until an acid reaction resulted; it was then mixed with a solution of acetate of lead; the liquid at first remained clear, but very soon the walls of the vessel were coated with a light white precipitate of a peculiar form; and the liquid very soon became troubled by a thick, flocculent, dazzling white, voluminous precipitate of the new lead salt, which quickly subsided, and was easily washed. The precipitate formed after drying a white light powder, insoluble in acetic acid, even on boiling with it.

The lead salt, dried at 212°, furnished on analysis—

Carbon	16·75	..	8 =	48	16·69
Hydrogen	2·90	..	8	8	2.77
Nitrogen	19·04	..	4	56	19·47
Oxygen	22·22	..	8	64	22·28
Oxide of lead	39·09	39·37	1	112	38·79

This new acid is consequently derived from allantoin by taking up 2 equivs. of water:—

2 equivs. of allantoin	$= C^8 N^4 H^6 O^6$
2 equivs. of water	$= H^2 O^2$
1 equiv. of hydallantoinic acid	$= C^8 N^4 H^8 O^8$

By treating the lead salt with sulphuretted hydrogen, the acid was obtained in the form of a colourless solution of a very acid taste; it could also be isolated by decomposing the lead salt with sulphuric acid.

The acid was evaporated in a water-bath to a thick syrup, which could not be crystallized; it was precipitated by absolute alcohol (in which the acid, and as it seems its salts, are insoluble) as a white brittle mass, which however very soon attracted moisture and deliqueseed; mixed with cold potash ley, ammonia was given off, and on evaporation some insoluble flocks separated; mixed with a drop of ammonia, and adding nitrate of silver, a white precipitate resulted, which dissolved for the greatest part by heating. With baryta water there was no precipitate, but after the addition of alcohol a flocculent white precipitate, which again disappeared upon the addition of water. Neutralized with ammonia and evaporated in the water-bath, ammonia escapes, and the solution again acquires its acid reaction; with chloride of barium, and the addition of ammonia, there is a white precipitate; with acetate of lead a thick white precipitate; mixed with carbonate of soda or potash, no carbonic acid was given off; on heating, the alkaline solutions became turbid, with separation of white flocks. These reactions, and especially the behaviour with alkalies and silver, indicated that the acid had already suffered an alteration by the heat during evaporation; nevertheless the silver salt was prepared from it, dried at 212° F., and analysed; the amount of oxide of silver was found to be 45·31, and by combustion with soda-lime 13·12 per cent. nitrogen were obtained; these numbers give a relation of equivalents of oxide of silver to nitrogen nearly as 2 : 5, which proves clearly that an alteration of the acid had taken place.

I did not follow this subject further, because it was less my intention to investigate the products of decomposition of allantoin, than to study the process of oxidation of uric acid by means of ferridcyanide of potassium and caustic potash. The similarity of these products, obtained by the decomposition of allantoin, with the allanturic acid obtained by Pelouze from the decomposition of allantoin by acids, is unquestionable; but a comparison of the analytical results was not possible, because in the paper of Pelouze on this subject the formula only, without the details of analysis, is given.—Silliman's *Journal*, November 1848.

On the Presence of Salicine and Carbolic Acid in Castoreum. *By* Prof. F. Wöhler.

The supposition, announced some time ago, that the odour of fresh castoreum might probably be owing to its containing a small quantity of carbolic acid, has been confirmed by experiment. This fact merits attention, since it has also been shown that carbolic acid is very poisonous*, and evidently acts in small doses as a neurotic. On this occasion another substance was discovered in castoreum, viz. salicine, the presence of which, as also that of the benzoic acid, which had been previously observed, may perhaps contribute to explain the physiological import of this organ, as these substances must undoubtedly be derived from the food of the Beaver.

* Chem. Gaz., vol. vi. p. 239.

The sac of *Castoreum Canadense* employed by me was decidedly genuine and uninjured. The mass contained in it was of a light yellowish-brown colour, homogeneous, soft, and possessed a strong odour. It was cut open and distilled with water; the distillate was clear, and contained only a few very small drops of oil; it had a strong smell of castoreum. With perchloride of iron it gave the characteristic reaction of carbolic acid very distinctly, although in a faint degree; it became violet, which colour again disappeared in the course of a short time with a whitish cloudiness precisely like carbolic acid. It was not coloured yellow by ammonia, as is the case with salicylous acid.

The liquid left in the retort was filtered boiling hot from the mass of castoreum. On cooling, it became turbid, and deposited a small quantity of a yellowish powder, the nature of which could not be ascertained. It was readily soluble in potash. It contained no uric acid; it is more likely to have been ellagic acid, as indicated by the colour with which it dissolved. The liquid filtered from it contained a salt of benzoic acid and salicine. On mixing it with muriatic acid, it became turbid, and deposited in the course of a day a considerable quantity of groups of small crystals, which, after rinsing and recrystallization, exhibited all the properties of benzoic acid. It was however remarkable that the mother-liquor separated from these crystals gave with perchloride of iron, at first a deep violet-blue colour, and only afterwards the white cloudiness peculiar to the benzoate of iron, a reaction which points to the presence of salicylous acid, and which was no longer produced by the recrystallized benzoic acid. Salicine does not furnish this colour. I have moreover ascertained by careful experiments that the benzoic acid was neither cinnamic acid nor hippuric acid, and could not have originated from the latter by decomposition.

The salicine remained in the muriatic solution from which the benzoic acid had separated. The muriatic acid was saturated with carbonate of baryta, the solution evaporated to dryness, and the dry mass extracted with alcohol. This left on evaporation a smeary semicrystalline mass, which, on distillation with chromate of potash and dilute sulphuric acid, gave an aqueous solution of salicylous acid, well-characterized by the odour, the yellow colour produced on saturating with alkalies, and by the dark violet colour on being mixed with perchloride of iron. Even the residual, soft, resinous mass afforded, on distillation with chromate of potash and sulphuric acid, a weak solution of salicylous acid.—Liebig's *Annalen*, lxvii. p. 360.

Researches on Proteine. *By* Prof. G. J. Mulder.

I last year stated that the sulphur and phosphorus might be contained as an organic group in albumen, caseine, &c., in combination with proteine; this statement may now be looked upon as confirmed. Proteine combines with different quantities of SNH^2 and PNH^2;

and the products of this union are albumen, hair, &c. Proteine also combines with oxygen, and forms another organic group, which likewise yields with SNH^2 and PNH^2 a class of bodies closely related to the above.

All former experiments confirm the fact, that sulphamide and phosphamide, in union with a single organic group, is able to form those substances which at present are called the albuminous bodies. Proteine itself, *i. e.* the organic group free from sulphur, can only be looked upon as an empirical expression; its difference from what was formerly termed proteine is explained by the elimination of nitrogen and hydrogen when an albuminous body is desulphurized. I formerly thought that only sulphur and phosphorus were removed in this process.

Consequently, to desulphurize albumen is to decompose the SNH^2 which occurs in it. This is accomplished with the formation of the elements of water, when the $2(SNH^2 + HO), 2NH^3$ which escape produce S^2O^2; and this latter combines to a greater or less extent with the proteine.

The dephosphorization of albumen results in a similar manner. PNH^2 furnishes with HO, NH^3 and PO, which combines with the potash employed for the dephosphorization.

It is therefore evident that there can no longer be a question of the existence of a proteine free from sulphur, as the quantity of S^2O^2 which existed, combined with the proteine obtained from different sources, may be increased and diminished, and even reduced to a minimum.

Desulphurization of Fibrine.—It may be considered as settled that albuminous bodies, when subjected to the influence of a hot solution of potash and exposed for some time to the atmosphere, produce, when mixed with acetic acid, a flocculent precipitate, which when heated with potash upon silver furnishes a stain of sulphuret of silver, and when boiled with a concentrated solution of potash does not exhibit the least coloration resulting from the formation of sulphuret of lead upon the addition of acetate of lead; but on burning this precipitate with nitre, it affords sulphuric acid, the quantity of which varies according to the different methods of preparing the substances and the different albuminous bodies.

I first attempted to determine the amount of sulphuric acid which is obtained from fibrine. For this purpose, I mixed the substance in a silver crucible with pure caustic soda, moistened the mass with just sufficient water to soften it, evaporated it at a gentle heat, and then calcined it until there was no further disengagement of hydrogen. I then added nitrate of potash until the whole formed a clear liquid, let it cool, and dissolved the mass in water rendered acid with a few drops of hydrochloric acid. The sulphuric acid was then precipitated by chloride of barium, and the amount of sulphur calculated from the sulphate of baryta. In this manner I obtained from fibrine 1·2 per cent. sulphur.

When fibrine was heated with a solution of caustic potash until the solution furnished very decided reactions of sulphur with acetate

of lead, and the liquid was exposed for some days to the atmosphere until the sulphur reaction had disappeared, one portion of the liquid was precipitated with acetic acid, another portion with oxalic acid, and a third with phosphoric acid. These precipitates, which exhibited not the slightest reaction upon silver foil, gave, on combustion with soda and nitrate of potash, a quantity of sulphate of baryta, the sulphur of which corresponded in the mean to 0·72 per cent. Fibrine therefore loses, on treatment with potash, about one-half its sulphur, and contains the other half in some form in which it does not act upon silver or lead.

Sulphurization of Fibrine.—To ascertain whether the organic group might be made to take up more than 0·72 per cent. of sulphur, and whether perhaps this quantity might be raised to the amount originally contained in fibrine, *i. e.* 1·2 per cent., I passed into a portion of the liquids of the preceding experiment, from which a part of the sulphur had been precipitated with acids, sulphurous acid until all the organic substance capable of being precipitated was thrown down; the washed precipitate was exhausted with alcohol. Another portion of fibrine was treated in the same manner with solution of potash, but with this difference, that sulphurous acid was passed immediately into the liquid, while it furnished a dark black colour with acetate of lead; this reaction of sulphur was soon removed by the sulphurous acid. The precipitate obtained with acetic acid was washed and treated as above.

According to the first method the amount of sulphur is increased to 1·16 per cent., which is the quantity originally contained in fibrine; by the second method it is increased to 1·49, which is very nearly the quantity occurring in albumen.

As the increase from 0·72 to 1·49 per cent. took place under circumstances which give rise to S^2O^2 (the liquid contains KS; consequently when SO^2 is passed through it, there is formed $2KS + 4SO^2 = 2KO + 3S^2O^2$) this increase can only be ascribed to hyposulphurous acid. If, moreover, we bear in mind that the liquids above mentioned originally contained KS, which must have become converted by the oxygen of the air into S^2O^2, we must ascribe to this not merely the increase of the amount of sulphur to 1·49 per cent., but also the 0·72 per cent. which occurs in the precipitate. The original form in which the sulphur is contained in the fibrine has nothing in common with that which has originated after the treatment with potash; the first forms sulphurets with silver and lead, whilst the latter has none of these properties.

Desulphurization of Albumen.—It was desired to ascertain accurately whether, in the treatment of albumen with potash, the amount of sulphur which is contained in the organic group, after the precipitation by acetic acid, in a form in which it does not react upon silver and lead, would correspond to the original quantity, or amount to more or less. I had on a former occasion found 1·38, 1·13, 1·38 per cent. sulphur in 100 parts of albumen, from an albuminate of copper. By fusion with soda and nitrate of potash I obtained 1·67 per cent. sulphur; but it results from further experiments, that

proteine from albumen only contains 1·6 per cent. of S when prepared with potash.

Albumen was dissolved in a solution of caustic potash in the manner above described, and at the same time a small quantity of phosphorus added, so that a small portion of phosphorus always remained undissolved; after the liquid had stood for four hours in the water-bath and been frequently shaken, it was filtered hot and precipitated with acetic acid. The precipitate furnished the same amount of sulphur as the proteine yielded which had not been treated with phosphorus.

On adding an excess of protochloride of iron to a similar solution of albumen in potash, and then adding a solution of potash to precipitate the whole of the iron, a considerable amount of sulphuret of iron was formed at the same time; the precipitate produced by acetic acid in the filtered liquid exhibited upon silver foil the reaction of sulphur, and contained 1·37 per cent.

A similar solution of albumen in potash was agitated with an excess of minium; the sulphuret of lead produced was separated from the liquid, which was freed from any sulphuret of lead in solution by the addition of some acetic acid and repeated filtration; it now furnished with acetic acid a precipitate which exhibited no reaction upon silver, and contained 1·48 per cent. of sulphur. Albumen, treated in the same manner with brown peroxide of lead, furnished a precipitate which contained 1·29 per cent. S.

It is evident, from these experiments, that proteine from albumen retains the same amount of sulphur = 1·6 per cent., only after treatment with potash, but in such a form that it cannot be detected with silver or lead; this quantity is not altered by deoxidizing substances such as phosphorus, whilst it is diminished by those substances which readily part with oxygen.

Sulphurization of Albumen.—Albumen was treated according to the same method as that described for the sulphurization of fibrine; the precipitate contained 1·55 per cent. sulphur, that is to say, the same quantity as would have been obtained without the use of sulphurous acid; SO^2 therefore does not increase (acting upon the KS, and producing S^2O^2) the amount of sulphur in the albuminous precipitate. The white of ten eggs was dissolved in caustic potash with 1 grm. of flowers of sulphur, digested in the water-bath, and then exposed to the air for four weeks until all reaction upon lead salts had disappeared. The precipitate produced with acetic acid contained 1·811 per cent. sulphur. Albumen treated in the same manner, but with the addition of 2 grms. of sulphur, gave a precipitate which contained 2·00 per cent. sulphur. 2 grms. proteine from albumen, which had furnished 1·57 per cent. S, were dissolved in a dilute solution of soda; the solution mixed with 0·5 NaO, S^2O^2, and precipitated with acetic acid, contained 1·77 per cent. of sulphur. The question, in what form the sulphur is contained in albumen, is difficult to answer; it appears most probable that the sulphur is held in solution as such in the acetic acid by the proteine; this rendered it impossible to increase the quantity of the

sulphur having no reaction upon silver and lead above 1·6 per cent. The question now arises, whether the amount of sulphur diminished to 1·29 can be increased again to 1·6 per cent.; if this is the case, it probably happens under circumstances in which only S^2O^2 can be formed; this would then throw some light upon these sulphur compounds; but an answer to the question could only be obtained by procuring albuminous proteine which should contain 1·29 sulphur, not reacting upon silver, dissolving it in potash, and precipitating it with acetic acid, or dissolving this proteine at the ordinary temperature in soda or potash, and adding some hyposulphite of soda. These experiments lead us to suspect that the whole of the sulphur contained in proteine, which does not react upon silver, is to be considered as existing in the state of S^2O^2.

Now if we consider the amount of sulphur to vary in albuminous proteine, it is evident that in the preparation of proteine some sulphur-compound has been eliminated and another taken up; it is proved that the last-added sulphur-compound is an oxide of sulphur, and most probably S^2O^2. Since the amount of sulphur in albuminous proteine varies between 1·6 and 1·3, some body must in the last case be mixed with it, which either contains no S^2O^2, or very little of it; we shall soon become acquainted with several other similar substances. If we calculate from the sulphur occurring in the albuminous proteine in the form of S^2O^2 the amount of this acid, we have in 100 parts—

	Maximum.	Minimum.
S^2O^2 =	2·40	1·95

Carefully-prepared chlorite of proteine contains sulphur, which does not act upon salts of silver or lead, while a combination of ClO^3 with albumen distinctly indicates this reaction; the chlorite of proteine contains 76·5 per cent. proteine, which on combustion with soda and nitrate of potash furnishes 1·22 per cent., or in 100 parts proteine 1·6 per cent. S. Chlorine, since it converts all albumen into chloro-proteine, furnishes a means of desulphurizing proteine, and is moreover well adapted for ascertaining more accurately the forms under which the sulphur occurs in albumen and the chlorite of proteine, both that which acts upon silver and that which does not. Chlorine consequently removes no sulphur from albumen; it is merely changed into the form S^2O^2.

Dephosphorization of Albumen and Fibrine.—Phosphorus, which occurs in combination with albumen and fibrine, can readily be removed by solution in hot caustic potash and precipitation with acetic acid; the precipitate contains not a trace of phosphorus, nor can the precipitate combine with phosphorus, as shown by one of the above experiments.

Composition of Albuminous Proteine.—The composition of the precipitate from albumen, which is obtained when albumen is dissolved in hot solution of potash, and the solution exposed to the air until it no longer gives the reactions of sulphur, and then precipitated with acetic acid, can only be correctly ascertained when,—1st, the sulphur which occurs in it is brought into calculation; and 2nd, attention is

paid to the form in which the sulphur is contained in it. This form is S^2O^2, but the quantity is variable. If the last trace of albumen has not been decomposed, and the whole of the proteine is not combined with S^2O^2, the N cannot possibly be correct, because SNH^2 are eliminated in the formation of proteine. Proteine from albumen, which furnishes 1·4 per cent. S as S^2O^2, gives no more than 14·4 per cent. N. The nitrogen of proteine is therefore too high in my experiments, as also in those of Scheerer, Dumas and Cahours.

Albuminous proteine, which did not act upon silver, left an unweighable quantity of incombustible residue, and gave in different experiments 14·12 and 14·23 per cent. N. Völcker found 14·0 to 14·4.

The proteine from albumen, which shows no reaction upon silver, and contains S^2O^2 in maximum, consists of C 53·7, H 7·0, N 14·2, O 23·5, S 1·6.

If we reduce these numbers by S^2O^2, that is to say calculate the sulphur as S^2O^2 and deduct it, we then obtain in 100 parts—

			Reduced by S^2O^2.
Carbon	53·7	53·7	55·0
Hydrogen	7·0	7·0	7·2
Nitrogen	14·2	14·2	14·5
Oxygen	23·5	22·7	23·3
Sulphur	1·6		
	100·0	97·6	100·0

This expression is, in my opinion, the true composition of a proteine perfectly free from sulphur; it differs from the former one by containing 1·5 per cent. less N. This error was not detected in my earlier determinations, because I considered all the combinations of albumen with tannic acid, sulphuric acid and chlorous acid as proteine compounds; but they are combinations of albumen, and consequently of proteine with SNH^2.

Composition of Albumen.—The composition of albumen and albuminous-proteine with S^2O^2 is—

	Albumen.	Proteine from albumen with S^2O^2.
Carbon	53·5	53·7
Hydrogen	7·0	7·0
Nitrogen	15·5	14·2
Oxygen	22·0	23·5
Phosphorus	0·4	
Sulphur	1·6	1·6

On comparing these numbers, it is seen that C and H remain unaltered, N has increased in the albumen, and O has become less; the phosphorus is eliminated, and the sulphur, on the conversion of albumen into proteine, has entered into a different combination. It appears that SNH^2 and PNH^2 separate, and that their place is occupied by S^2O^2. When albumen is reduced by the two first substances, we obtain the same organic group, which makes its ap-

pearance when proteine from albumen with S^2O^2 is reduced by S^2O^2:—

	Egg-albumen reduced by SNH^2 and PNH^2.			Proteine from albumen reduced by S^2O^2.
Carbon	53·5	53·5	55·6	55·0
Hydrogen	7·0	6·8	7·1	7·2
Nitrogen	15·5	13·9	14·4	14·5
Oxygen	22·0	22·0	22·9	23·3
Phosphorus	0·4			
Sulphur	1·6			
	100·0	96·2	100·0	100·0

The analysis of the albumen from the serum of the blood furnishes the same result, which may be expressed by

$$C^{36}H^{27}N^4O^{12} = C^{36}H^{25}N^4O^{10} + 2HO.$$

A proteine containing 2·4 per cent. sulphur is represented by $5C^{36}H^{27}N^4O^{12} + S^2O^2$; while albumen, in which only sulphur is admitted into the formula, may be expressed by $5C^{36}H^{26}N^4O^{11} + 2SNH^2$.

The formula of this albumen would be $20(C^{36}H^{26}N^4O^{11}) + 8SNH^2 + PNH^2$. It consists in 100 parts of—

Sulphamide	3·2
Phosphamide	0·6
Hydrate of proteine	96·2

[To be continued.]

ANALYTICAL CHEMISTRY.

On the Analysis of Compounds containing the Oxides of Iron and Manganese, Alumina and Alkaline Earths in combination with Phosphoric, Arsenic and Silicic Acids. *By* R. Fresenius.

I. *Separation of the Peroxide of Iron from Phosphoric Acid in the presence of Alkaline Earths.*

a. Many chemists have hitherto assumed, that by fusing the perphosphate of iron with carbonated alkali and exhausting the mass with boiling water, the perphosphate of iron may be completely separated from phosphoric acid (Berzelius, Rammelsberg); nay, that even when alkaline earths are present, the phosphoric acid passes entirely to the alkali, and is dissolved on treatment with water (Rose).

I had formerly convinced myself that phosphate of lime and phosphate of magnesia could not be perfectly decomposed with carbonate of soda; but now I have found that even the peroxide of iron cannot

be wholly deprived of phosphoric acid by this treatment. In fact, if the residue, after being most carefully washed, is dissolved in muriatic acid, precipitated with ammonia and sulphuret of ammonium, filtered, and the solution mixed with chloride of ammonium and sulphate of magnesia, there is always obtained a very perceptible precipitate of ammonio-phosphate of magnesia; it consequently requires no further proof that all the methods based upon the above principle are inaccurate.

b. When a muriatic solution containing phosphoric acid, peroxide of iron and lime, is mixed with carbonate of soda until the free acid is nearly saturated, then mixed with an excess of acetate of soda and boiled, the whole of the phosphoric acid is precipitated with the peroxide of iron, whilst the lime remains in solution. The peroxide of iron and phosphoric acid may then be separated by sulphuret of ammonium. This method is not inaccurate, but it is extremely inconvenient, especially when mere traces of phosphoric acid have to be estimated and the amount of peroxide of iron is very great, a case which very frequently occurs in the analysis of iron ores, soils, &c.

With respect to the other method, which is given in my Introduction to Quantitative Analysis, of separating phosphoric acid from peroxide of iron (it consists in adding tartaric acid, and then ammonia, to the solution, and lastly a mixed solution of chloride of ammonium and sulphate of magnesia), I must observe that it has now been found to lead to erroneous results; as a mixture of a solution of tartaric acid, sulphate of magnesia, chloride of ammonium and ammonia deposits after a short time, when of a certain degree of concentration, a crystalline precipitate, which has entirely the appearance of the ammonio-phosphate of magnesia. The employment of citric acid, sugar, &c., instead of the tartaric acid, has not yielded satisfactory results.

c. The method which I now employ is based upon an entirely new principle. The solution, which we will suppose to contain much peroxide of iron, lime and some phosphoric acid, is heated to boiling, removed from the lamp, and a solution of sulphite of soda added until the colour has become pale green, and carbonate of soda produces a white precipitate; it is then boiled until the smell of sulphurous acid has disappeared, any excess of free acid neutralized with carbonate of soda, a few drops of chlorine water mixed with it, and lastly an excess of acetate of soda. The smallest quantity of phosphoric acid is immediately detected by the production of a white flocculent precipitate of perphosphate of iron*. [This reaction is so sensitive because the perphosphate of iron is insoluble both in acetic acid and in the acetate of the protoxide of iron, whilst it dissolves abundantly in a solution of the peracetate of iron. It is owing

* When the solution contains silicic or arsenic acid, a precipitate is formed in the absence of phosphoric acid. These two acids must therefore be first separated, before the phosphoric acid can be detected with certainty by the above reaction. See Course of analysis, p. 22.

to this circumstance that no precipitate is ever obtained when a nearly neutral solution of the peroxide of iron, containing only a small amount of phosphoric acid, is mixed with acetate of soda; the blood-red liquid remains clear in the cold, and the whole of the iron, with the phosphoric acid, is only deposited on boiling.] Chlorine water is now added gradually until the liquid appears reddish; it is then always turbid. It is boiled until it has become clear, which soon results, filtered hot, and the precipitate washed with hot water. This precipitate contains the whole of the phosphoric acid as perphosphate of iron mixed with a minute quantity of basic peracetate of iron; the solution contains nearly the whole of the iron and the lime, which are easily separated by sulphuret of ammonium. The precipitate containing the phosphoric acid and iron may be readily and completely decomposed, after solution in muriatic acid, by the addition of ammonia and sulphuret of ammonium. But perfect decomposition may also be effected in the following manner, avoiding the use of sulphuret of ammonium. It is dissolved in muriatic acid, reduced with sulphite of soda as above, an excess of caustic potash or soda added, boiled until the precipitate has become black and granular, and then filtered through very close paper*. This precipitate is protoperoxide of iron free from phosphoric acid; it is dissolved in muriatic acid, and united with the other solution of iron. The filtered solution contains the phosphoric acid, which is precipitated in the usual manner as ammonio-phosphate of magnesia.

II. *Separation of Iron from Alumina.*

One of the most frequent operations of analytical chemistry is the separation of peroxide of iron from alumina by caustic potash; it is however very inaccurate. It had already been noticed by several persons, that the separation of these two oxides by caustic potash was not complete; and Knop† has in consequence proposed precipitating the solution with sulphuret of ammonium, and then boiling with potash. This latter method is however extremely inconvenient, as the liquid, even though yellow and free from iron at the commencement, almost always passes through green and ferruginous in the washing, whether pure water or water containing sulphuret of ammonium is employed. The following experiment will show the inaccuracy of the usual method. A solution of chloride of aluminum, containing 1·000 grm. alumina, was mixed with a solution of perchloride of iron, an excess of caustic soda added to it, boiled, filtered hot, the filtrate acidified with muriatic acid, and carefully precipitated with ammonia. After standing several hours in a warm place, it was filtered. The alumina upon the filter was yellow, and led me to suspect the presence of iron, which was subsequently confirmed.

* When the filter is too porous, very often some of the fine precipitate passes through, especially when washed. Should this happen, the filtrate is suffered to stand, the clear liquid decanted, and the remainder filtered through a separate little filter.

† Chem. Gaz., vol. v. p. 14.

The hydrated peroxide of iron also contained alumina, since although completely washed it gave a precipitate, although a very small one, on being again boiled with caustic soda and treating the filtrate as above. Instead of 1·000 grm. alumina, only 0·909 (which moreover contained iron) was obtained; there was consequently a loss of 10 per cent. After standing for eight days, the filtered solution deposited some alumina; consequently the whole of the lost alumina had not remained with the iron, but a portion had not been precipitated by the ammonia. After some experiments the cause of it was found out. It is owing to the circumstance, that, on filtering the liquid containing the caustic alkali through paper, organic matter is dissolved, which prevents the precipitation. This was proved by the following experiments:—

A solution of pure chloride of alumnium, containing 1·320 grms. alumina, was precipitated with potash, the precipitate redissolved in an excess of potash, the liquid heated to boiling, filtered, acidified with muriatic acid, and precipitated with ammonia. The alumina obtained amounted only to 1·290, that is 97·72 per cent. In a second experiment, made in the same manner, instead of 2·640 grms. only 2·590 or 98·48 per cent. were obtained. This evil is avoided by filtering through asbestos instead of paper; but far more simply and better by heating the liquid acidified with muriatic acid, and boiling with a little chlorate of potash (upon the addition the flask is removed from the fire). By this means the organic substance, preventing the complete precipitation of the alumina, is destroyed, as the following experiments will show. A solution containing 0·3420 alumina was treated as above described; after being acidified with muriatic acid, boiled with chlorate of potash, it gave 0·3418 grm. alumina, that is 99·94 per cent. In a second experiment, instead of 0·150, 0·1495 or 99·67 per cent. were obtained.

The other source of inaccuracy, which in the first experiment had raised the loss of alumina to 10 per cent., and which is owing to its not being possible to free the hydrated peroxide of iron completely from alumina by caustic potash, may be avoided without the application of Knop's inconvenient method. The acid solution, containing the alumina and peroxide of iron, is heated to ebullition in a flask, removed from the fire, and reduced with sulphite of soda. The liquid, after being kept boiling for some time, is neutralized with carbonate of soda, an excess of caustic soda added, and, after being well-shaken, boiled until the liquid has become black and granular. [The succussion which precedes the boiling may be avoided by inserting a coil of platinum wire, and also by constant agitation. As soon as it really boils the thumping ceases.] It is now removed from the fire and allowed to subside, the clear liquid passed through a close filter, and the precipitate washed with hot water, at first by decantation, and then upon the filter. The filtered solution, treated in the above-mentioned manner with muriatic acid and chlorate of potash, furnishes, upon precipitation with ammonia and several hours' standing, *the whole* of the alumina in a perfectly pure state.

III. *Separation of Alumina from Phosphoric Acid.*

To make an accurate analysis of a compound containing alumina, peroxide of iron, lime, magnesia and phosphoric acid, it is necessary, in the first place, to separate the alumina from the other bases. This is readily effected by precipitating the liquid, after the peroxide of iron has been reduced by sulphite of soda, with carbonate of soda, and then boiling with the addition of an excess of caustic soda. It must be borne in mind, in this case, that, on boiling, the carbonic acid which had been combined with the protoxide of iron passes to the soda, which it converts into carbonate; consequently, to retain the alumina in solution, it is requisite to add from time to time some caustic soda, and especially when the precipitate has become black and granular. In this way the alumina, together with *a portion* of the phosphoric acid, is obtained in solution (when alumina and peroxide of iron are the only bases present, *the whole* of the phosphoric acid is in the filtered solution), and we have now to seek for a simple method of separating the two.

The following furnishes perfectly satisfactory results:—The alkaline solution is rendered acid, boiled with some chlorate of potash, precipitated with ammonia (avoiding a large excess), and chloride of barium added as long as a precipitate appears. After digesting for some time, it is filtered. The precipitate, which contains the whole of the alumina and phosphoric acid (the latter combined in part with alumina and in part with baryta), is collected upon a filter, washed with a little water, and dissolved in as little muriatic acid as possible. The solution is saturated with carbonate of baryta with the assistance of heat, an excess of caustic soda added, and heat applied. Any baryta contained in the solution is precipitated by carbonate of soda and filtered. The whole of the alumina is now in the solution, and the whole of the phosphoric acid in the precipitate. The solution is rendered acid with muriatic acid, boiled with chlorate of potash, precipitated with ammonia, allowed to stand for some hours in a warm spot; the alumina filtered, washed, dried, calcined and weighed. The precipitate is dissolved in muriatic acid, and the baryta precipitated with dilute sulphuric acid, separated by filtration, and the phosphoric acid determined as ammonio-phosphate of magnesia as usual.

IV. *Course of Analysis.*

The compound, the analysis of which we will describe, I will suppose to contain a large amount of peroxide of iron, protoxide of manganese, alumina, lime, magnesia, phosphoric acid, sulphuric acid, arsenic acid, silicic acid and sand, as is the case with iron ores.

A weighed quantity (which should not be too small) of the finely-pulverized mineral is digested with moderately-dilute muriatic acid in a flask, at a temperature near to boiling-point, until all that is soluble has passed into solution. The liquid is diluted, passed through a filter of known weight of ash, and the residue washed. With brown iron ore the quantity is in general very small. It is dried

with the filter, carefully separated from it, calcined and weighed; it is then transferred into a boiling solution of carbonate of soda, allowed to boil for some time, filtered through the filter first employed, washed, dried, calcined and weighed. The difference between this weight (sand, alumina, &c.) and the one first obtained gives the amount of insoluble residue, or silicic acid.

The ferruginous muriatic solution is filtered from the residue, carefully evaporated to perfect dryness, and kept for some time at a temperature slightly above that of boiling water. After it has been moistened with muriatic acid, and kept for some time with it at a gentle heat, water is added, and any silica separated by filtration. Its weight, added to that above obtained, gives the total amount of silicic acid in combination.

The ferruginous solution is heated to boiling in a flask, and reduced with sulphite of soda as described under I. When the whole of the sulphurous acid has been expelled by boiling, sulphuretted hydrogen is passed into the liquid until it is saturated with it. The precipitate produced is the protosulphuret of arsenic. The amount of arsenic contained in it is ascertained, after deducting the sulphur in it, which has been previously determined as sulphate of baryta, from its weight determined at 212°. If the precipitate does not appear yellow, but brown or black, there is reason to suspect some other metallic oxides, and it must be further examined in the ordinary manner.

The liquid filtered from the protosulphuret of arsenic is boiled to expel the whole of the sulphuretted hydrogen, then precipitated with carbonate of soda, and boiled with an excess of caustic soda (as directed in II.) until the precipitate appears black and granular. It is allowed to subside, the clear liquid poured off, the precipitate washed by decantation with hot water, and finally brought upon a filter of close texture, and washed with hot water.

a. Treatment of the Precipitate.—The precipitate (which contains protoperoxide of iron, protocarbonate of manganese, carbonate and phosphate of magnesia) is again transferred, together with the filter, into the flask, and digested with muriatic acid. After standing for some time in a warm place, it dissolves entirely, although not so readily as the hydrated peroxide of iron. When no more black particles are perceptible, it is filtered; the filter is left whole, a little hot water poured over it, the flask inclined so that it remains hanging to the side, and the liquid runs off, &c. In this manner it may be quickly and completely washed. The filtered solution is reduced with sulphite of soda, nearly neutralized with carbonate of soda, heated to boiling, mixed with a few drops of chlorine-water, then with an excess of acetate of soda; and when the liquid or the precipitate has not a reddish tint, chlorine water is added until this is the case. The whole is boiled until the precipitate has separated, filtered hot, and the precipitate, consisting of phosphate and some basic acetate of the peroxide of iron, washed.

α. The filtered solution is precipitated, after the addition of ammonia and while hot, with sulphuret of ammonium, filtered quickly,

the precipitate consisting of protosulphuret of iron and manganese, washed uninterruptedly with hot water, and the lime in the solution determined by oxalate of ammonia; and, after removing the oxalate of lime, the magnesia thrown down by phosphate of soda. The precipitate of the sulphurets is dissolved in muriatic acid, oxidized with chlorate of potash or nitric acid, boiled until all the chlorine is expelled, allowed to cool to about 140°, nearly neutralized with carbonate of soda, the peroxide of iron precipitated with carbonate of baryta, and the other oxides estimated in the usual manner.

β. The precipitate, containing the perphosphate of iron is dissolved in muriatic acid, reduced with sulphite of soda, boiled for some time with an excess of caustic soda, and filtered. The solution containing the phosphoric acid is supersaturated with muriatic acid, and placed aside. The precipitate of protoperoxide of iron is also dissolved in muriatic acid, oxidized with nitric acid, the solution added to the principal solution of the iron, separated from the manganese and baryta, and the whole precipitated with ammonia.

b. Treatment of the filtered Alkaline Solution.—This liquid, which contains the alumina, is treated exactly as described under III. The alumina is consequently weighed in a pure state. The solution, freed from baryta and containing phosphoric acid, is united with the abovementioned liquid containing the other portion of phosphoric acid, supersaturated with ammonia, and precipitated with sulphate of magnesia, with the addition of chloride of ammonium if necessary.

The sulphuric acid in the mineral is determined in a separate portion by dissolving it in muriatic acid, filtering the dilute solution, and precipitating with chloride of barium.

How far the course of analysis is simplified when one or the other of the substances in question is not present, I have not considered necessary to mention, nor the mode in which the qualitative examination should be conducted. I will only observe, with respect to the latter, that the course of analysis proposed cannot be deviated from without disadvantage; and further, that it is of great importance, before commencing the qualitative analysis, to ascertain the presence or absence of alumina, manganese and alkaline earths; for when no alumina is present, the first precipitation with carbonate of soda and the boiling with caustic soda may be omitted; the whole of the phosphoric acid is contained in the alkaline liquid holding the alumina in solution when no alkaline earths are present; and the residue which had remained undissolved by the potash may be at once treated for the separation of the iron from manganese; or, when no manganese is present, precipitated at once with ammonia from the muriatic solution after previous oxidation, calcined, and calculated as peroxide of iron.

In proof of the accuracy of this method, the author prepared a liquid containing known quantities of peroxide of iron, alumina, lime, magnesia and phosphoric acid, and divided it into two equal portions, each of which was analysed precisely according to the preceding directions. Each half of the liquid contained—

		Found.	
	Grms.	I.	II.
Phosphoric acid.....	0·100	0·0993	0·0995
Lime	0·133	0·1328	0·1327
Magnesia	0·103	0·1020	0·1029
Peroxide of iron	1·443	1·4426	1·4424
Alumina	0·150	0·1495	0·1495
	1·929	1·9262	1·9270
Or in 100 parts—			
Phosphoric acid.....	5·18	5·14	5·16
Lime	6·89	6·88	6·88
Magnesia	5·34	5·29	5·33
Peroxide of iron	74·81	74·78	74·77
Alumina.....	7·78	7·75	7·75
	100·00	99·84	99·89

Journ. für Prakt. Chem., Nov. 1, 1848.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On a New Instrument for ascertaining the relative Quantities of two liquids when mixed together, and particularly mixtures of Alcohol and Water, by the dilatation of those liquids. By J. T. Silbermann.

Various means have been suggested and employed for ascertaining the respective quantities of alcohol and water in mixtures of those liquids; but these are all found to possess many disadvantages. I have the honour to propose to the Academy a method which has not hitherto been employed for this purpose, by which the evils attendant upon the other plans are obviated.

The processes hitherto known are founded either upon the distillation, density, or boiling-point of the alcoholic liquid. Now, mine is based upon the *dilatation* of the alcoholic liquid. It is well known that between zero and 100° Cent. of temperature the dilatation of alcohol is triple that of water. This dilatation is still greater between 25° and 50° of temperature, and may be thus demonstrated:—Pour water, at 25°, into a thermometer, so as to fill the reservoir, and a small portion of the tube up to a certain mark; then, on heating the thermometer to 50°, the water will rise a certain distance above the mark; and let this rise be marked on the tube. Now, if the same quantity of pure alcohol, also at 25°, be substituted for the water, and heated to the same temperature (viz. 50°), it will be found to have risen $3\frac{1}{2}$ times higher than the water. Any mixture of alcohol and water, on being treated in the same way, will be found to have a mean point of dilatation between these two, and will be nearer the

one or the other, according as either liquid preponderates in the mixture. If, therefore, a series of mixtures of alcohol and water be made, beginning with water 100 parts, alcohol 0; water 99, alcohol 1; water 98, alcohol 2; water 97, alcohol 3, &c., up to water 0, alcohol 100; and their several points of elevation, at the respective temperatures of 25° and 50°, be carefully marked on the tube, a complete centesimal alcoholometric scale will be produced, which will indicate the quantity of alcohol contained in any mixture of alcohol and water, by introducing it at 25°, and afterwards heating it up to 50°.

The same process may be employed with any other two liquids having points of dilatation differing from those of alcohol and water; but it will be understood, that the same scale will not serve for more than one mixture. In order to adapt this principle to the ordinary purposes of alcoholometric measurement, I have constructed a thermometer in a peculiar manner,—thereby forming an instrument which I call a *dilatometer*. The form and arrangement of this apparatus are as follows:—To a metallic plate are fixed two thermometers, one of mercury, marked with the initial and final temperatures (say 25° and 50°), and the other, for containing the liquid to be tested, is open at top and bottom, tapered at the lower end beneath the reservoir and terminating above in a large tube; it is in fact a species of funnel.

As the alcoholometric scale is above the point where water stopped at 50°, the portion intended for the dilatation of pure water may be replaced by a space of equal capacity, *i. e.* shorter but wider, consisting of an enlargement in the interior at that part. The tube is thus shortened, and the number of its divisions for other purposes may be increased. The thermometer for holding the liquid is closed at its tapered point below by a small valve of cork, suitably fixed on a spring, which is fastened to the supporting plate.

In order to cause the liquid under examination to flow, the spring-valve is depressed by means of a copper rod, attached to the supporting plate by a clamp-piece (in a position to act upon the spring), and to the top or funnel-shaped part of the thermometer by a nut, fitting on the upper part of the rod. In order to obtain a quick motion, the screw has four threads: to open or close the thermometer, it is only necessary to turn the head of this rod either in one direction or the other. As the liquids are often impregnated with air or gas, it is found necessary, before testing the liquids, to drive off the gas or air; the best method of effecting this is by means of a vacuum, which may be produced by the use of a small leather piston, working in the tube of the thermometer. This piston serves first, by suction, to fill the thermometer from below; and then, the lower part being closed and the piston driven down, on raising it the air will be seen to separate from the liquid at all points; and, after two or three more strokes of the piston, the liquid may be completely purified, so that no more bubbles will rise during the operation, having a tendency to disturb the column. To effect this withdrawal of the piston without any shock, so as not to divide the co-

lumn abruptly, the piston-rod is made hollow throughout; the operator, having wetted his finger, applies it to the top of the piston-rod, in order to create a vacuum as he draws up the piston; he then removes it to re-admit the air, and the piston is thus removed without a shock. In order to form the vacuum properly, the liquid must be pumped in until it rises through the piston-rod on depressing the piston; on seeing this, the operator may be sure that, on raising the piston, there is no air left underneath it. The tube is now full of liquid, and by depressing the spring-valve the liquid is run off, until it is only as high as the lowest mark on the tube, when the temperature has been for two or three minutes at the lowest degree of the mercury thermometer.

I propose this new method, as the old processes possess certain inconveniences, which I will briefly point out.

Distillation.—This process is but very rarely employed, as it is a very long operation and requires great skill. Its adaptation is owing to the ingenious methods of M. Gay-Lussac, which had simply for their object the discovery of the truth, without regard to the time required for arriving at a conclusion.

Density.—The errors in this process result from mixing the liquid with salts or syrups, the specific gravity of which, being greater than that of alcohol, prevents its true quality from being ascertained; thereby facilitating the evasion of the excise duties and the cheating of the purchaser. Wines, for the same reasons, only indicate about one-half their strength. For this reason M. Gay-Lussac, in such cases, combines his distilling process with his alcoholometric areometer.

Boiling-point.—Of all the known processes conducted on this principle, M. Tabarié has incontestably introduced the best; but experienced persons are aware of the difficulties to be met with in determining this point; they know that steam or vapour may be heated beyond its point of generation, and that the thermometer, even when immersed in the liquid, may, under certain circumstances, stand several degrees above the real temperature, which will give an error of four alcoholometric degrees for every extra degree of temperature. Besides this, it is necessary to take the barometric variations into account in some better way than has been hitherto done.

The process which I propose, and which is based upon the principle of dilatation, may be applied to test wines as well as alcoholic liquids of any strength; for the salts and vegetable substances, in solution, which enter into their composition in combination with water and alcohol, do not materially affect the result, as all solutions expand in the same degree as water within the range of temperature which I have chosen. There is no occasion to fear the presence of any liquid more dilatable than alcohol, as liquids of such a nature are more expensive, and may besides be detected by their peculiar smell or taste. The same reasoning is also applicable to liquids less dilatable than water. I have chosen 25° as the initial temperature, because water may always be found below that temperature in summer.

With regard to the final temperature of 50°, I have chosen that temperature to avoid the effect of evaporation, which might diminish the actual degree, if it approached too near the boiling-point; and as respects the range between this and 25° I have found it sufficient. Besides, these two temperatures offer great facilities for the experiment, as, if it be conducted in a vessel capable of containing about a quart of water, a small spirit-lamp underneath will be sufficient to maintain either of these temperatures. The plate, carrying the thermometers, serves to agitate the water, in order that its temperature may be uniform throughout.—*Comptes Rendus*, Oct. 23, 1848.

PATENT.

Patent granted to Thomas Richardson, Newcastle-upon-Tyne, *for Improvements in the Manufacture of Manure.*

This invention consists in manufacturing manure by dissolving animal matters, containing phosphates of lime and magnesia, in the liquor of the alum-works, known as "salts-mothers," or in a solution of "rough Epsoms."

The animal matters, such as bones or guano, are mixed with a small proportion of nitrate of soda, potash, lime or magnesia, or nitric acid, in an iron pan lined with sheet lead, and heated from below; then a certain quantity of the salts-mothers or solution of rough Epsoms (as hereafter mentioned) is added, and the whole boiled until the animal matter disappears. The pan should be about 18 feet long, 6 feet broad and 18 inches deep. The quantity of the phosphates of lime and magnesia contained in the animal matters must be first ascertained; and then to every 75 lbs. thereof should be added 100 gallons of salts-mothers or 300 lbs. of rough Epsoms (dissolved in as little water as possible), with a quantity of one of the above-mentioned nitrates, depending upon the nature of the animal matters operated on. When bones are used, the nitrate or nitric acid is to be employed in the proportion of 1 lb. to every 26 lbs. of the bones; but only half the proportion will be necessary when treating guano. The animal matter is to be reduced to powder under a pair of edge-stones previous to being mixed with the other materials.

The patentee states, that to œconomize fuel, a portion of rough Epsoms may be dissolved in the salts-mothers, as a substitute for the latter, in the proportion of about 3 lbs. of rough Epsoms for every gallon of salts-mothers.

The liquid in which the animal matter has been decomposed will present the appearance of a thick magma; it should be evaporated to such a consistence as will admit of its being removed to a drying floor; and then the remainder of the water is to be expelled at a temperature which should never rise sufficiently high to injure the animal matter. The patentee prefers a temperature of about 300° F. When dry, the manure is ground to powder, and is then ready for use.—Sealed May 26, 1848.

THE CHEMICAL GAZETTE.

No. CL.—January 15, 1849.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Researches on Proteine. *By* Prof. G. J. Mulder.

[Concluded from p. 18.]

On the change which Albumen experiences by Potash and Chlorine.

It is well known that albumen, when treated with a solution of potash, disengages ammonia at an elevated temperature. Chlorine, passed into albumen, precipitates all the albumen; the precipitate contains the whole amount of sulphur, but in a form in which it does not act upon silver. The liquid is found to contain chloride of ammonium; consequently ammonia is the only substance which is formed and has separated from the compound. The action of potash and of chlorine is readily explained; if we assume sulphamide to exist in albumen, ammonia is liberated by chlorine, but the amount of sulphur remains unaltered, and has only assumed the character of an oxyacid, S^2O^2. The chlorine consequently liberates the sulphamide, and forms $2NH^3 + S^2O^2$ from $2SNH^2 + 2HO$. The action of potash on albumen is twofold; SNH^2 yields, under the influence of KO and HO, $2H^3N + S^2O^2$, of which the ammonia escapes, whilst part of the latter combines with the potash and a part with the precipitate produced by acetic acid. The formation of KS may be explained from the hyposulphites being decomposed by heat, KO, S^2O^2 forming KS.

With regard to the presence of sulphamide in albumen, it is not necessary to prove the isolated existence of this group. With respect to the question, whether the sulphur in the proteine, which does not act upon silver, is contained in it as S^2O^2, and not as SO^2 or SO^3, it may be answered, that there is not a single reason in favour of its being SO^3; but it is certainly an oxide of sulphur, and everything leads us to admit S^2O^2, and not SO^2.

With respect to the phosphamide, it may be observed that the phosphorus in fibrine and albumen exists in two different states; it is partly combined with lime as PO^5, and can be removed by muriatic acid; but a part is contained in a different form, as the amount of phosphoric acid obtained by decomposition with nitric acid is always greater than by means of muriatic acid. That this phosphorus occurs in the state of phosphamide is proved from the evolu-

tion of phosphuretted hydrogen on precipitating proteine with acetic acid from the potash solution. This subject will be noticed at length under legumine, which contains the largest amount of phosphorus.

Action of Sulphurous Acid upon Albumen.—The effect of sulphurous acid, like that of potash, atmospheric air and chlorine, is to cause the albumen no longer to act upon salts of lead and silver. Albumen from an egg, treated in an alkaline solution with sulphurous acid, furnished a precipitate which contained 2·22 per cent. sulphur; the precipitate had consequently absorbed by means of the sulphurous acid 0·6 per cent. of sulphur.

Quick method of preparing Proteine containing S^2O^2.—Albumen is dissolved in caustic potash, kept from three to four hours in the water-bath until it acts strongly upon a salt of lead; sulphurous acid is then passed through the warm mass until some proteine is precipitated. From the liquid filtered from this, acetic acid precipitates proteine, which contains exactly 2·4 per cent. S^2O^2; this proteine is of a pure white colour, possesses all the properties of that found nine years ago, and exhibits the most perfect agreement with albumen.

Substance precipitated with the Proteine and soluble in Alcohol.—In the ordinary method of preparing proteine with S^2O^2 from albumen, there is at the same time precipitated a substance which is soluble in alcohol; its quantity is most considerable in caseine. This substance dissolves in boiling alcohol, and again separates for the greater part on cooling. The boiling alkaline solution of this substance, obtained from albuminous proteine, leaves on evaporation a body which, after it has been freed from fat by treatment with æther, presents all the properties of proteine. This body is converted by nitric acid into xanthoproteic acid, and furnishes with hydrochloric acid the violet substance of Bourdois and Caventou.

The Liquid from which Proteine has been precipitated in the Treatment of Albumen with a hot Solution of Potash.—This liquid contains various substances; in the first place an organic substance, soluble in water, which possesses the general properties of proteine, but contains less S^2O^2. When chlorine is passed into the liquid, precisely the same organic group is obtained as is contained in the precipitate with acetic acid. If the liquid acidified by acetic acid is saturated with potash and acetate of copper added, a slight precipitate is obtained, and the liquid filtered from it gives no precipitate with potash, but remains clear and becomes violet, as in the treatment of grape-sugar with copper salt and potash; sugar of gelatine exhibited precisely the same reaction.

Salts of Proteine and of Proteine Compounds.—The properties of the salts of proteine and those of albumen are nearly identical. It is evident, from a large number of experiments, that albumen acts a double part, that of a base and of an acid. The quantity of the base is very small, and at present the preparation of pure albuminates of the metallic oxides is not conceivable, as these bodies contain several impurities. Proteine is likewise not perfectly free from fixed substances. I have not analysed the salts in which proteine plays the part of an acid; but they may easily be prepared, as an

alkaline solution of proteine furnishes abundant precipitates with metallic salts, which however only contain from 2 to 3 per cent. oxide. It is different with the acids; the capacity of saturation of albuminous proteine and of albumen is very nearly the same.

Sulphate of Proteine and Sulphate of Albumen.—As the amount of S^2O^2 in proteine and SNH^2 in albumen, which remains in combination after the action of sulphuric acid, is not accurately known, the atomic weight of proteine from albumen can only be deduced approximatively from the combination with sulphuric acid. These compounds were decomposed with muriatic acid; sulphate of albumen was composed of,—C, 50·1; H, 6·9; N, 14·9; O S, 19·8; SO^3, 8·3. Sulphate of crystalline gave 8·63 per cent. SO^3, and sulphate of caseine 8·45; this composition gives the following formula:— $C^{36}H^{25}N^4O^{10} + (0{\cdot}4\ SNH^2) + SO^3, HO$.

To prepare the combination of proteine with sulphuric acid, albuminous proteine, containing 1·6 per cent. S in the state of S^2O^2, was conveyed into pure SO^3, HO, and left in contact with it until the substance had perfectly dissolved to a thick yellowish liquid; it was then poured into a large quantity of water, when it was precipitated as a white powder, soluble in alkalies, and resembling in its behaviour the sulphate of albumen; its composition may be expressed by the formula $2\ (C^{36}H^{27}N^4O^{12}) + SO^3$.

Muriate of Albumen and Muriate of Proteine.—When muriatic or sulphuric acid is added to a solution of albumen, fibrine or caseine, a combination of the organic substance with the acid employed is precipitated. The muriatic compound was found to contain 3·6 to 3·8 per cent. ClH. Its composition is 5 equivs. albumen and 2 equivs. ClH.

Tannate of Albumen and Tannate of Proteine.—When tannic acid is dropped into a compound of proteine with S^2O^2, tannate of proteine containing the entire amount of S^2O^2 is obtained; but if tannic acid is mixed with albumen, tannate of albumen containing SNH^2 is obtained. Proteine, like gelatine, combines with different quantities of tannic acid. It results from all the experiments, that albumen cannot be distinguished from proteine by its atomic weight, but only by its reactions.

Action of Chlorine upon Albumen.—When chlorine is passed into a clear aqueous solution of albumen, a flocculent precipitate is formed, which varies according to the length of time the chlorine is allowed to act upon it; when the action is not continued too long, it consists of a combination of albumen with chlorous acid, but after a longer reaction, of a combination of proteine with chlorous acid and hyposulphurous acid.

Chlorite of Albumen is represented by the formula $C^{36}H^{25}N^4O^{10} + (0{\cdot}4\ SNH^2) + ClO^3, HO$. 1 equiv. water has been eliminated, and its place taken by ClO^3.

Chlorite of Proteine, $C^{36}H^{25}N^4O^{10} + 0{\cdot}2\ S^2O^2 + 2ClO^3$; at 212° this substance loses half the ClO^3.

The action of chlorine upon the proteine compounds appears to throw most light upon our knowledge of proteine; the organic group

containing these bodies constantly yields $C^{36}H^{25}N^{4}O^{10}$, and the whole of the proteine which was contained in the original substance is received into the chlorine compound. Moreover, chlorine is a very excellent means of decomposing sulphamide and phosphamide, and depriving all the proteine substances of the reaction of sulphur.

Oxyproteine.—Hitherto this name was applied to a substance which is obtained as a second precipitate from the potash solution of hair, after the proteine has first been precipitated and separated by filtration. Excess of acetic acid then furnishes a second precipitate of a substance insoluble in water, which has many properties in common with fibrine. This substance has, according to analysis, the formula $C^{36}H^{27}N^{4}O^{12} + O$, and it should be called protoxyproteine instead of the name it has hitherto had of binoxyproteine.

Vitelline is a combination of this oxyproteine with sulphamide; it contains sulphur in the form in which it reacts upon silver. When protoxyproteine is submitted to the action of chlorine, it behaves exactly like proteine.

With regard to *caseine*, it has been found to consist of a mixture of different proteine compounds; the same applies to *crystalline*, which must be equally submitted to further examination.

Oxyproteine from Fibrine.—When perfectly white well-washed fibrine from ox-blood is treated with a dilute solution of potash, and in the same manner as for the preparation of proteine, it furnishes a substance which has retained the character of fibrine, and contains more oxygen than proteine. It is perfectly white, and has most of the properties of proteine; it did not react upon silver foil, and was insoluble in alcohol; its formula is $C^{36}H^{27}N^{4}O^{12} + O$.

Tritoxyproteine.—When ammonia is poured over chlorite of proteine, it dissolves, with disengagement of nitrogen; if the liquid is evaporated to dryness and the residue exhausted with alcohol, chloride of ammonium and the substance insoluble in alcohol, tritoxyproteine, are obtained. This substance may be obtained in a purer state by boiling albumen, fibrine, &c. with water, and exhausting with alcohol the residue obtained on evaporation. The decomposition in the preparation from the chlorite of proteine by means of ammonia is that from $C^{36}H^{25}N^{4}O^{10}$, $C^{36}H^{25}N^{4}O^{10} + ClO^{3}$ is formed; and this on solution in ammonia furnishes chloride of ammonium and $C^{36}H^{25}N^{4}O^{13}$, with disengagement of nitrogen. In the formation of this body there is always a little hydruret of benzoyle evolved; this point may enable us to ascertain the constitution of proteine; it merits therefore to be more closely examined.

Horny Tissues.—Hair, horn and whalebone, which were formerly classed amongst the proteine compounds, favour the view that in general the albuminous substances consist of a combination of sulphamide with proteine. Laer, Tilanus and Kerckhoff have shown that they all furnish oxyproteine on treatment with a hot solution of potash, and some even proteine. I am not yet in a condition to state accurately which of these bodies contain proteine and which oxyproteine. In the cellular contents of these tissues small quantities of substances occur which modify the composition of the cell-

wall and interfere with the results of the analysis. 100 parts whalebone contain 7·2 parts sulphamide, 100 parts hair 10 parts sulphamide, and 100 parts of cow's horn 6·8 parts sulphamide. Tortoiseshell is a mixture, and does not belong to the simple proteine substances; skin is nearly related to horn, but I had not sufficient at my disposal to repeat the determination of the sulphur; the former statement is undoubtedly too low. The author then draws the following conclusions:—

1. The albuminous substances which have as yet been examined may be regarded as combinations of $C^{36}\,H^{25}\,N^{4}\,O^{10}$ with sulphamide and phosphamide in different proportions.

2. Others, which are closely related to the above-mentioned substances, are $C^{36}\,H^{25}\,N^{4}\,O^{4}$ and $C^{36}\,H^{25}\,N^{4}\,O^{13}$, and may be called oxyproteine.

3. Sulphur is not an essential constituent of the precipitate which acetic acid produces in a solution of albuminous substances; in warm potash it varies in amount, and it is contained in the form of $S^{2}\,O^{2}$. —*Journ. für Prakt. Chem.*, vol. xliv. p. 488.

On the Combinations of Platinum with Nicotine. *By* M. Raewsky.

From the author's experiments it results—

1. That in the action of nicotine upon the protochloride of platinum two new compounds are formed, one of which is represented by the formula

$$PtCl\,C^{10}\,H^{7}\,N,\,2KCl,$$ orange-coloured salt;

the other by the formula

$$PtCl\,C^{10}\,H^{7}\,N,\,KCl,$$ red salt.

2. That the orange-coloured salt exhibits numerous instances of isomerism according to the nature of the solvent employed; with respect to the red salt, only one compound is known to be isomeric with it.

3. That no compounds occur in this series analogous to the salts of MM. Reiset and Magnus, and that in this respect nicotine cannot be compared to ammonia.

4. That the red salt is analogous to the dark red compound of platinum and aniline, $PtCl\,C^{12}\,H^{7}\,N,\,KCl$, in which nicotine is replaced by aniline.—*Comptes Rendus,* Dec. 11, 1848.

On a new method of preparing Collodion. *By* M. Lepage.

The author has observed that gun-cotton dissolves as readily in a mixture of equal parts of sulphuric æther and alcohol of 0·863 spec. grav. as in pure æther, and that the collodion obtained with this mixture is quite as adhesive as that prepared without the use of alcohol. As it dries less rapidly in the air, this property may in certain cases render it preferable to the ætherial solution of gun-cotton.—*Journ. de Pharm.*, Dec. 1848.

On some Products resulting from the Action of Alkalies and Acids upon Aldehyde. By H. WEIDENBUSCH.

As regards the action of alkalies, the author has in general confirmed the observations of Liebig concerning the resin of aldehyde thus produced; it was found impossible to determine its composition by experiment, owing to its want of stability. In the action of potash upon aldehyde, there is observed, according to Liebig, a very irritating odour; this belongs, according to the author, to a volatile oily substance, which is very quickly altered in the air, and is finally converted into an apparently different resin from the true aldehydic resin. When this oil is isolated, it is thick, of a golden colour, with an agreeable cinnamon-like odour; it dissolves in alcohol and æther, and is somewhat soluble in water. Nitric acid effects the oxidation more quickly than the air. The oil adheres so tenaciously to the resin, that it may be boiled for days without losing its odour.

The author obtained the resin in the form of a bright orange product, which became paler by long drying at 212°. It dissolves in alcohol, æther, and somewhat in water. Alkalies scarcely dissolve it; it dissolves partially in concentrated sulphuric acid, from which water again precipitates it. When dissolved in alcohol, a few bubbles of chlorine passed through the solution decolorize it completely, so that water precipitates now a snow-white powder; however, the precipitate contains chlorine. The analyses of the resin, purified as carefully as possible, furnished 76·40 per cent. carbon, 7·97 hydrogen, 21·63 oxygen. The author did not notice any inflammation of the resin, as observed by Liebig.

It is evident, from the small amount of oxygen contained in this resin, that, on the decomposition of aldehyde, some substances containing more oxygen must be produced. On examining the alkaline liquid, acetic and formic acids were found; moreover, some reactions observed by the author clearly point to the presence of acetylous acid.

Action of Acids upon Aldehyde.—Little more was known on this subject than that aldehyde is converted into acetic acid by nitric acid, and is blackened by sulphuric acid. When pure aldehyde, mixed with about half its volume of water, is mixed with a trace of sulphuric or nitric acid, the vessel being cooled below 32°, fine acicular crystals soon separate, and the supernatant liquid has lost its odour of aldehyde, and is no longer miscible with water. The reactions of the crystals indicated the non-fusible modification of the metaldehyde described by Liebig.

The liquid above the crystals was decanted and agitated with water, to remove any undecomposed aldehyde; the liquid, thus purified and floating on the water, was dried by means of chloride of calcium. This product is a

New Modification of Aldehyde, $C^4 H^4 O^2$, which agrees in composition and density of vapour with that described by Fehling, but possesses different properties. It is a thin limpid liquid, of a peculiar aromatic odour and burning acrid taste, soluble in alcohol and

æther, and also somewhat in water. It boils at 257°, and distils over unaltered. It changes alone, and also with water, rapidly into an acid, the liquid in the water gradually decreasing; crystals frequently separate from the water. It is not altered by potash. It is especially remarkable, that when this liquid is heated with a trace of sulphuric acid, it is reconverted into aldehyde. The same acid therefore which at low temperatures converts aldehyde into this new modification, produces at higher temperatures a reconversion into aldehyde. Nitric acid behaves in the same manner; it is consequently impossible to look upon the action of these acids in any other light than as a dynamic one; for the acids exist unaltered in the liquids, and can be detected by reagents. The author has not yet determined the nature of the acid into which this new modification of aldehyde is changed. It is formed only by exposure to the air, and not by alkalies or oxidising agents. Alkalies do not appear to exert any action upon the liquid. On saturating a small quantity of the liquid which had become acid in the air, a crystallized salt of baryta was obtained, which dissolved easily in water, readily reduced salts of silver, and gave a white precipitate with proto- and persalts of mercury. The former is reduced on heating to metal, but the latter remains white even on boiling.

For analysis, the last portions, which passed over and which were free from unaltered aldehyde, were employed. The results obtained were—

						Calculated density of vapour.
Carbon.....	54·15	54·35	4	24	54·55	3 vols.=2·52837
Hydrogen.....	9·13	9·11	4	4	9·09	6 0·41280
Oxygen.....	36·72	36·54	2	16	36·36	1½ 1·65390
	100·00	100·00		44	100·00	

The density of the vapour, determined by experiment, amounted to 4·5830.

Action of Sulphuretted Hydrogen upon Aldehyde.—When sulphuretted hydrogen is passed through a mixture of aldehyde and water, the liquid becomes turbid; and when saturated, deposits at the bottom of the vessel a thick transparent oil. The gas must be passed in for a very long time, as the oil is not easily deposited from an imperfectly saturated liquid. It is separated by decantation from water, the last traces of which are removed *in vacuo*, as it is decomposed by chloride of calcium and other dehydrating agents even in the cold. With chloride of calcium it yields sulphuret of calcium, with evolution of aldehyde. This oil is composed of $C^{12}H^{13}S^{7}$ = 3 atoms of an aldehyde in which the oxygen is replaced by sulphur + 1 atom of sulphuretted hydrogen. It forms a thick limpid liquid, with an intense disagreeable odour of garlic, which adheres most tenaciously to the hands and clothes. It is somewhat soluble in water, readily so in æther and alcohol, and miscible with fatty and essential oils. Although it does not begin to boil before 356°, yet it evaporates quickly, and fills every place with its most unsup-

portable odour. Heated in a retort, it boils at 356°; but the boiling-point constantly rises, and the oil acquires a brown colour; and finally a brown smeary mass is left in the retort, which on cooling solidifies to a cake of crystals of the acetylic mercaptan described below. The specific gravity of the oil is 1·134. It afforded on analysis—

Carbon	36·37	36·14	12 =	72	36·54
Hydrogen	6·67	6·70	13	13	6·59
Sulphur	56·43	56·74	7	112	56·35

This oil is decomposed by ammoniacal gas and thialdine produced, 3 equivs. sulphuretted hydrogen being eliminated, and 1 equiv. ammonia absorbed. Evidently the conjunct, which with ammonia forms the base $C^{12} H^{10} S^4$, is momentarily produced in this reaction. The nauseous odour of the oil changes, on passing ammonia into it, into that of aldehyde-ammonia; the liquid becomes milky, and after several days the beautiful rhombic crystals of thialdine separate. The muriate, which was quickly obtained by passing muriatic gas into the oil saturated with ammonia, after it had been dissolved in æther, in which the muriate of thialdine is insoluble, was taken for analysis; it gave—

Carbon.....	35·73	12 =	72·0	36·10
Hydrogen	6·90	14	14·0	7·02
Nitrogen	7·16	1	14·0	7·02
Sulphur	31·79	4	64·0	32·09
Chlorine	17·53	1	35·4	17·77

Acetylic Mercaptan, $C^4 H^4 S^2$, a body which, from its composition (but not in its reaction towards peroxide of mercury), stands in the same relation to aldehyde as mercaptan to alcohol. It is formed from the oil just described in various ways, for instance when the oil is exposed to the air, when it is heated, and also under the influence of acids. If the oil is placed in a watch-glass over sulphuric acid under a bell-glass, the acid turns brown, and the sides of the glass become gradually coated with crystals of acetylic mercaptan. It is therefore impossible to deprive the oil of water in this way.

A few bubbles of chlorine passed into the oil act like muriatic and sulphuric acids, *i. e.* they likewise separate $C^4 H^4 S^2$; but this substance again disappears with more chlorine, and an oily liquid with an unsupportable odour is produced, which undoubtedly contains chlorine and sulphur.

Further, if a drop of concentrated sulphuric acid be added to the oil, it instantly solidifies to a white crystalline mass, and sulphuretted hydrogen is evolved. More sulphuric acid dissolves these crystals, producing a transitory brown colour, but water precipitates them again. Muriatic acid acts in a similar manner to sulphuric acid; and when passed in the state of gas through the oil, causes it to congeal to a solid cake of crystals. This body contains no oxygen, but in its place sulphur; it is formed from the oil by 1 atom sulphuretted hydrogen separating from the compound $C^{12} H^{13} S^7 - HS = 3C^4 H^4 S^3$.

Acetylic mercaptan crystallizes in dazzling-white shining needles, of a disagreeable garlic odour; at 113° they begin to sublime, and then separate in loose flaky masses like snow. This compound dissolves in alcohol and æther, and somewhat in water, and distils over with the latter, upon which it floats. From its alcoholic solution it first separates on the side of the vessel in beautiful dendritic crystals.

Acetylic mercaptan is not altered by ammonia or potash. When nitric acid is poured over it, it effervesces violently, and probably yields, analogous to mercaptan and amylic mercaptan, a conjugate sulphuric acid, which however was not further examined.

When this substance is treated with salts of silver, the whole of the sulphur is not obtained as sulphuret of silver; but the crystalline mass combines with nitrate of silver to a salt of definite composition. The sulphur was therefore determined by mixing the substance with nitrate and carbonate of soda, and heating in a combustion-tube. Analysis gave—

Carbon.....	39·44	39·64	4 =	24	40·00
Hydrogen	7·10	6·87	4	4	6·67
Sulphur	53·05	53·40	2	32	53·33

A *compound*, $C^6 H^6 S^3 + AgO, NO^5$ or $3(C^4 H^4 S^2) + 2AgO, NO^5$, *i.e.* of acetylic mercaptan with nitrate of silver, is obtained by mixing an alcoholic solution of acetylic mercaptan with an alcoholic solution of nitrate of silver; a tolerable thick white precipitate falls, which quickly changes its colour. When it is heated it shrinks considerably, black flakes of sulphuret of silver separate, and the hot alcohol contains the silver compound in solution; it is filtered boiling, when it separates immediately, partially even upon the filter, in nacreous laminæ, which after some time settle at the bottom of the vessel, forming a soft precipitate. It is therefore advisable to dilute the alcohol with some water, in which mixture the salt is more easily soluble, and so to prevent the too quick separation of the crystals.

This salt forms a delicate white powder, consisting of minute crystalline scales; it becomes dark by exposure to the light, and has the smell of acetylic mercaptan. When heated it yields nitrous acid and blackens, probably with formation of sulphuret of silver. On decomposition in a retort with alkalies, acetylic mercaptan sublimes or distils over. It dissolves only in boiling absolute alcohol, but in cold alcohol the more readily the more dilute it is. This salt exhibits considerable resemblance, as regards its formation and external appearance, to that which is produced by nitrate of silver in a solution of aldehyde-ammonia. Like that it is decomposed on evaporating its solution, depositing black sulphuret of silver. This compound is however peculiar; for there is no other example of an oxyacid, for as such the nitrate of silver must be looked upon, entering into combination with a sulpho-base as acetylic mercaptan.

From the chemical behaviour of this body, the second formula given above seems to express the composition of this compound, the atomic weight of which at the same time confirms the rational com-

position of acetylic mercaptan = $C^4 H^4 S^2$. Powerful bases separate the latter from this compound. The analysis of the salt gave—

Carbon	13·49	13·52	12 =	72	13·84
Hydrogen	2·45	2·77	12	12	2·31
Sulphur.....	18·26	18·53	6	96	18·46
Oxide of silver	44·77	44·59	2	232	44·63
Nitric acid.....	20·88	20·86	2	108	20·76

In conclusion, the author makes a few observations upon the constitution of acetylic mercaptan, aldehyde and ethyle. Löwig and Weidmann obtained, by treating the oil from olefiant gas with sulphuret of potassium, the monosulphoetherine, or elaylic mercaptan. The formula given by Löwig and Weidmann has been doubled by Gmelin = $C^4 H^4 S^2$, in order to make it agree better with that of the Dutch oil, $C^4 H^4 Cl^2$. This renders acetylic mercaptan isomeric with that body; whence it would result that Dumas and Boulley's view, according to which æther is the hydrate of olefiant gas, cannot be correct, since the body prepared from olefiant gas has totally different properties to that prepared from aldehyde. Although this furnishes no proof of the existence of the radicals ethyle or acetyle, Liebig's view, according to which acetyle must be looked upon as the basis of the ethyle compounds, obtains further support by a comparison of these isomeric sulphur compounds; and on this very account they deserve more accurate investigation. The author endeavoured to deprive the body $C^4 H^4 S^2$ of 1 equiv. sulphuretted hydrogen; but this did not succeed any more than depriving aldehyde of 1 equiv. water, for the purpose of reconverting it into the lowest oxide of acetyle.—*Ann. der Chem. und Pharm.*, xxvi. p. 152.

On the Gum Kino of the Tenasserim Provinces.
By the Rev. F. Mason.

In a valuable article by Dr. Royle on Gum Kino, reprinted in the Journal of the Agricultural and Horticultural Society of India, which ostensibly enumerates all the various regions from which it has been imported into England, there is no mention of this article being imported from this coast. Yet long before Dr. Royle compiled that communication, more than one consignment had been made by parties in Maulmain to houses in London of gum kino to the amount of a thousand pounds.

It was brought to Maulmain by an English merchant from the Shan States, and stated by him, as our commissioner at the time informed the writer, to be the production of the *Pa-douk*, the same tree as the one in Maulmain thus denominated by the Burmans. Several years before I had directed attention to this tree as producing an astringent gum resembling gum kino, but the medical officer to whom I submitted specimens of the gum said it was "a kind of dragon's blood;" but after it was known that the gum of the Pa-douk had been sold in London for the veritable gum kino, another medical gentleman tried in his practice the exudation of the

tree in his compound in the place of the gum kino in his stores, and reported the effects the same, that their medical virtues were alike.

The next inquiry that arises is for the genus and species of the Pa-douk. When I first came to the coast, all the English residents of my acquaintance called it "Burman Senna," and the surgeon of the station told me that he believed it was a species of senna. The Rev. H. Malcom, D.D., President of Georgetown College, Kentucky, who came out to India a dozen years ago in order to go back again and write a book, has stereotyped in his travels,—"Pa-douk, or Mahogany (*Swietenia Mahogáni*), is plentiful in the upper provinces, especially round Ava, found occasionally in Pegu." In a native Pali dictionary, found in the Burmese monasteries, Pa-douk stands as the definition of *Pe-tá-thá-lâ*, and the corresponding Sanscrit word in Wilson's Dictionary is defined *Pentaptera*; but the Pa-douk does not belong to that genus. In Piddington's Index however *Peetshala* stands as the Hindee name, and in Voigt's Catalogue *Peet-sal* as the Bengalee name of *Pterocarpus marsupium*; and this brings us nearer the truth, for Pa-douk is a name common to two different species of *Pterocarpus*, but which look so much alike that they are usually regarded as one species. Undoubtedly one species is *P. Indicus*, and the other I presume is the one named by Wight *P. Wallichii*, but which was marked in Wallich's Catalogue *P. Dalbergioides*, from which it differs in no well-marked character excepting that the racemes are axillary and simple, while in the latter they are terminal and "much-branched." Wight says of *P. Wallichii* in his Prodromus, "stamens all united or split down on the upper side only;" so they are sometimes in our tree. In the figure that he gives in his Illustrations they are represented as diadelphous, nine and one, and so they are seen occasionally in our tree; but the more common form is that of being split down the middle into two equal parts, of five each, as in *P. Dalbergioides*. The wood too resembles it. "Not unlike mahogany, but rather redder, heavier and coarser in the grain." It is often called "red wood" at Maulmain; and from the colour of the wood, some of the natives distinguish the species "red Pa-douk," being *P. Dalbergioides*, and "white Pa-douk," *P. Indicus*.

Both these trees produce an astringent gum, which has been exported for gum kino; or whether it was a mixture of both it is not possible to say. Probably the latter, as the native collectors would not probably make any distinction. Possibly it is the production of neither. It may be that *P. marsupium* is found in the Shan States, for it grows I believe in Assam; and the man that did not distinguish the two species in Maulmain, would not distinguish them from a third at Zimmay. Be that as it may, this is certain, that these provinces can furnish the commercial world with a large quantity of gum kino. If the result of the experiment which was made be correct, we have a great abundance of it within our own borders; for the Pa-douk is one of the most common forest trees in the provinces from the Tenasserim to the Salwan. It furnishes a considerable

portion of the fuel that is sold in Maulmain. But if not, it is certainly abundant in the neighbouring provinces, whose only avenue to market is through our territories.—*Journal of the Asiatic Society of Bengal*, August 1848.

On the Composition of the black Precipitate which is formed at the Anode in the decomposition of Sulphate of Copper by the Galvanic Current. By Maximilian Duke of Leuchtenberg.

Sand, 1·90; antimony, 9·22; tin, 38·50; arsenic, 7·40; platinum, 0·44; gold, 0·98; silver, 4·54; lead, 0·15; copper, 9·24; iron, 0·30; nickel, 2·26; cobalt, 0·86; vanadium, 0·64; sulphur, 2·46; selenium, 1·27; oxygen, calculated for the metallic oxides and loss, 25·14 = 100.

Silver, gold, platinum, copper and some iron could be extracted from the black precipitate by amalgamation; it must therefore contain, besides the noble metals, a portion of the copper in the unoxidized state, which however most probably becomes mixed with it mechanically on cleansing the anode from the precipitate, which weakens the current very considerably.—*Bullet. de St. Pétersb.*, No. clviii. p. 218.

On the ripening of Fruits and the Gelatinous Bodies of Vegetables. By E. Fremy.

The author gives the following summary of the facts detailed in his memoir on the above-named subjects:—

1. There exists in the tissues of vegetables, and principally in the pulps of fruits and of roots, a substance insoluble in water, which he has named *pectose*; its characteristic property is that of being converted into pectine, by the influence of the weakest acids. It differs essentially from cellulose in all its properties.

2. Pectine exists in the juices of ripe fruits; it may be artificially obtained by causing boiling weak acid liquors to act upon pectose. Pectine ought to be considered as a weak acid; it does not precipitate the neutral acetate of lead, and changes into pectic acid under the influence of soluble bases.

3. Pectine, submitted for some time to the action of boiling water, acquires the property of precipitating neutral acetate of lead, and is converted into a new substance which M. Fremy calls *parapectine*; it is neutral to test-papers, and occurs in the juices of perfectly ripe fruits.

4. Parapectine is transformed, under the influence of acids, into a substance which the author calls *metapectine*; it has the properties of a weak acid, reddens tincture of litmus, and precipitates chloride of barium; it may be named *metapectinic acid.*

5. The preceding substances form compounds which are soluble in a certain number of acids, and principally with sulphuric and oxalic acids. These compounds are crystallizable, and form gelatinous precipitates with alcohol.

6. There accompanies pectose in vegetable tissues, a peculiar ferment called by M. Fremy *pectase*; this has the property of transforming pectine successively into two gelatinous acids, which are the pectosic and pectic acids; this change occurs without the presence of air or the disengagement of gas, and constitutes the *pectic fermentation*, which may be compared to the *lactic fermentation*. Pectase exists in vegetables in two states, one soluble and the other insoluble.

7. When pectine is submitted to the action of pectase, the acid first formed is a new acid, the *pectosic*; it differs from pectic acid in being completely soluble in boiling water.

8. Pectosic acid is transformed into pectic acid by the prolonged action of pectase; the pectosic and pectic acids are also formed when pectine is added to an alkali either free or carbonated, or under the influence of lime, barytes, or strontia.

9. Pectic acid dissolves in considerable quantity in neutral alkaline salts, and especially in ammoniacal salts, which contain an organic acid; gelatinous double salts with an acid reaction are then formed, which are precipitated in a gelatinous state by alcohol.

10. Pectic acid, kept for several hours in boiling water, completely dissolves, and is transformed into a new acid, the *parapectic acid*.

11. Parapectic acid changes, under the long-continued influence of water, into a powerful acid, the *metapectic acid*.

These two last acids arise under several circumstances, and principally by the reaction of acids, alkalies, or of pectase, pectine and pectic acid; they possess the property of decomposing by ebullition the double tartrate of potash and copper, like glucose.

12. Gelatinous substances exposed to a temperature of 392° Fahr. disengage water and carbonic acid, and are converted into a black pyrogenous acid, which the author calls *pyropectic acid*.

13. Gelatinous substances exhibit all the generic characters of acids, the capacity of saturation and their power augmenting in proportion as they recede from pectose; they appear to be all derived from a ternary molecule $C^8 H^5 O^7$, and differ from each other only as to water.

14. The properties of the gelatinous substances of vegetables afford an explanation of the alterations which a fruit undergoes when submitted to the action of heat, as well as of the formation *vegetable jellies*. Vegetable jellies may be produced—1st, by the conversion of pectine into pectosic and pectic acids under the influence of pectase; 2ndly, by the combination of pectic acid with the organic acids contained in fruits.

15. The pectose contained in green fruits is successively transformed, during ripening, into pectine, metapectine, and metapectic acids. These changes are determined by the influence of acids and pectase.

It will appear from this summary, in the opinion of the author, that after having ascertained the nature of the principal properties of the substances which constitute the pulp of certain fruits, he was led to observe that the gelatinous substances of vegetables undergo

modifications by the influence of reagents entirely comparable to those to which they are subject during vegetation.—*Ann. de Ch. et de Phys.*, Septembre 1848.

ANALYTICAL CHEMISTRY.

On the Estimation of Bromine in Salt Springs. *By* H. Fehling.

Bromine can only be detected in the brines by concentration and by the formation of mother-liquors; a quantitative determination of the bromine in the brines would prove very inaccurate, from the extremely minute quantity present. Even in the leys, this estimation, according to the usual method, by heating the chloride and bromide of silver in chlorine and ascertaining the loss, is not very accurate; for if the chloride of silver contains but mere traces of bromide, the loss is small in proportion as there is less bromide of silver in the mixture; and the result is rendered unsatisfactory by the unavoidable error of observation. If, for instance, 5 grms. of the silver precipitate decrease when heated in chlorine only, 1 milligrm., the result is already uncertain, and it can only be regarded as approximative, for $\frac{1}{4}$ milligrm. more or less makes a difference of 50 per cent.; but if the difference in weight of the chloride of silver before and after treatment with chlorine is still less, the result is too inaccurate to be regarded even as approximative; it is then without any value. Bromine could be detected in the leys examined; but its quantity was in general so very small, that the usual methods of estimating it were useless. The brines contained bromine; but its determination is still more uncertain, for even the precipitate obtained from the mother-liquors exhibited at the most only a difference of 0·005 to 0·001 grm. No result of any value could be obtained in this way. I therefore tried the plan proposed by Heine*, of setting the bromine free by chlorine, dissolving it in æther, and judging of the amount of bromine from the depth of the colour. For this purpose it is first necessary to procure a test-liquor containing a definite amount of bromine. I found by preliminary experiments that the mother-liquors under examination contained at the most 0·020 grm. bromine in 60 grms. I therefore prepared ten different liquors, each consisting of 60 grms. of a saturated solution of pure chloride of sodium†, which contained from 0·002 to 0·020 grm. bromine‡ (increasing 0·002 for each), in the form of bromide of potassium, which had furnished in numerous experiments 62·3 per cent. bromine.

* Chem. Gaz., vol. iv. p. 103.

† I employed a saturated solution of chloride of sodium instead of water, as Heine recommends, because the water diminishes the volume of the æther by solution, and so alters the intensity of the colour.

‡ To avoid the error which might arise in weighing such minute quantities of bromide of potassium, 1 grm. bromide of potassium, = 0·623 bromine, was weighed off, formed into any given volume of solution, and the requisite quantity of this solution by measure added to the solution of pure chloride of sodium.

An equal volume of æther was now mixed with the test-liquors, and then a certain measure of chlorine water; the quantity of the latter must be regulated by that of the bromine, for too much or too little of the chlorine is equally injurious, as the colour in both cases appears fainter than with the requisite quantity.

But since it is important to attain precisely this point of deepest colouring, I take from two to three glasses of the test-liquor of the same strength, and mix these gradually with different quantities of chlorine until the colour is seen not to become darker. This colour now serves for comparison. In this manner a scale of colours is prepared of progressively-increasing tint. 60 grms. of each of the mother-liquors under examination were now filled into glasses, and so that two or three glasses contained the same mother-liquor, which was then mixed with the same volume of æther as the test-liquor, and with the requisite amount of chlorine. The comparison of the colour of the æther of the mother-liquor with that of the test-liquor gives accurately the amount of bromine present to within 1 or 2 milligrms. (*i. e.* to $\frac{1}{60000}$ or $\frac{1}{30000}$). It is requisite to repeat the experiments several times, in order to obtain from the agreement of the results certainty as to their correctness. It hardly need be stated that the experiment must be concluded as quickly as possible after the chlorine has been added to the liquids containing bromine, and direct sun-light must be avoided; I preferred making my experiments with a clouded sky. When the glasses are all filled with the solution of salt or with mother-liquors, and mixed with æther, the experiment is soon finished with the aid of an assistant; and the saving in time which this method affords is a great advantage, as frequent repetition is necessary to be convinced of the accuracy of the results. When I observed all the precautions with regard to the quantity of chlorine to be added, quickness in executing the operation and avoiding a strong light, I always obtained the same results. At first I was erroneously led to admit less bromine than was actually present, especially in liquors which contain much bromine, owing to not having added a sufficient quantity of chlorine water. To check the results obtained by this method, I tried the fractionated precipitation of the chlorine, as directed in Rose's 'Manual of Analytical Chemistry,' when all the bromine is said to be contained in the last portion of the precipitate. I employed for this purpose 100 grms. of mother-liquor, and each time added one-tenth of the silver solution requisite to precipitate the whole; when eight-tenths had been precipitated, it was collected on a filter, washed, &c., and then the filtered solution wholly precipitated. After fusion both precipitates were treated with chlorine; it was found that the last precipitate lost nothing in chlorine in weight, even after a two hours' treatment; on the other hand, the first precipitate decreased decidedly as much or rather more than the chloride of silver, which had been obtained from another quantity of liquid precipitated entirely at once. I then examined whether any bromine is precipitated with the first portions of silver from a concentrated solution of chloride of sodium; and this I found to be the case in several experiments, so that 0·00001 bromine

can be determined in this manner. According to the electro-chemical theory, nearly the whole of the chloride of silver should be precipitated before any bromide is formed; that the contrary takes place is probably owing to the greater insolubility of the bromide of silver in a concentrated solution of chloride of sodium.

That in this way the bromide of silver may be as it were concentrated, and bromine separated from large quantities of chloride of sodium, is evident from the following experiments:—300 grms. of a solution of chloride of sodium were mixed with 0·460 bromide of potassium = 0·2865 bromine, amounting therefore to nearly 0·001. The whole of this liquid was now mixed in the cold with one-sixth the quantity of solution of silver requisite to precipitate the whole, shaken, filtered and washed. The filtered solution was again concentrated, precipitated with a sufficiency of a solution of silver, and this repeated a third time. In this manner I obtained three precipitates, which I shall call *a*, *b* and *c*, the total amount of which was about one-fourth what the solution of salt would have yielded had the whole been precipitated. These precipitates weighed after fusion,—*a*, 27·525; *b*, 10·336; and *c*, 6·374 grms.

A portion of the fused precipitate was now transferred into a reduction-tube, all moisture expelled by heat in a current of dry air; then, after weighing, fused and treated repeatedly with dry chlorine until the weight remained unaltered after half an hour's action of the chlorine. [With large quantities of bromine it was frequently requisite to treat the precipitate repeatedly with chlorine, each time from twenty to thirty minutes, to decompose it entirely; while a single treatment of from fifteen to twenty minutes sufficed for a few milligrammes of bromine.]

The above precipitates furnished the following results:—

5·490 grms. silver precipitate of *a* lost altogether					0·033 grm.	
5·474	...	...	..	...	0·029	...
4·236	...	...	...	...	0·025	...
15·200 grms. silver precipitate lost therefore....					0·087 grms.,	

which amounts for 27·525 silver precipitate to 0·1575 loss = 1·7957 × 0·1575 = 0·2828 grm. bromine*.

4·714 grms. of *b* did not lose in weight after two hours' treatment of chlorine; *c* behaved in the same manner. The loss in weight in this case touches only the sixth part of the precipitate, and is consequently six times as great as if it had been distributed over the entire precipitate; the error possible is so much the smaller. I moreover made the following experiments with solutions of different degrees of strength.

1·100 solution of chloride of sodium, mixed with 0·036 bromide of potassium (=0·0225 grm. bromine), contains $\frac{1}{50{\cdot}000}$ bromine. I

* The equivalent of bromine, divided by the difference between the equivalents of bromine and chlorine = $\frac{80}{80-35{\cdot}45} = \frac{80}{44{\cdot}55} = 1{\cdot}7947$.—Rose's *Manual*, vol. ii. p. 572.

then precipitated in the cold 24·654 grms. chloride of silver, and subsequently 16·398 :—

5·555 grms. of *a* lost		0·004
5·507	...	0·002
5·658	...	0·003
16·720 grms. lost		0·009 = 0·016 grm. bromine.

24·654 grms. chloride of silver contain therefore 0·0236 grm. bromine.

In a second experiment with the same state of dilution, 1000 grms. chloride of sodium solution were mixed with 0·02243 grm. bromine, and from the solution 15·545 grms. *a* and 21·035 grms. *b* chloride of silver precipitated :—

4·899 grms. of *a* lost	0·0035
4·754 ..	0·00425
9·653 lost.....	0·00775 grm.,

or 15·545 grms. lose 0·0125 grm. = 0·0224 bromine. The weight of precipitate *b* was not altered in chlorine.

Even when the amount of bromine is not more than $\frac{1}{100000}$th of the liquid, serviceable results are obtained. 2000 grms. of the solution of chloride of sodium were mixed with 0·0206 grm. bromine, and then 21·466 grms. *a* and 16·938 *b* precipitated from it :—

5·383 grms. of *a* lost altogether			0·003 grm.
6·150	...	...	0·0033 ...
11·533 lost therefore.....			0·0063 grm.,

which for 21·466 grms. chloride of silver amounts to 0·0117 grm. = 0·021 grm. bromine; the weight of *b* was not diminished in chlorine.

From these experiments it is evident that the amount of bromine may be very accurately determined even in liquids which do not contain more than 0·001 to 0·00001; and that even an approximatively accurate result may be obtained with still smaller quantities of bromine; however, the estimation of such minute quantities of bromine are rarely of any value. With more than $\frac{1}{1000}$th bromine the usual method is sufficiently accurate. I should also mention that the precipitate from this concentrated solution of chloride of sodium, when only a portion is thrown down, requires to be washed very long; in general from two to three days were requisite; that it should be precipitated in the cold; and that a comparatively greater portion of chlorine should be precipitated the larger the amount of bromine.

When the amount of chlorine was about $\frac{1}{1000}$th, I used from one-fifth to one-sixth of the silver solution requisite to precipitate the whole; with—

0·0001	bromine about	$\frac{1}{10}$th	of the requisite quantity of the silver solution.		
0·00002	...	$\frac{1}{30}$th	.	..	...
0·00001	...	$\frac{1}{60}$th	...	...	...

It is very possible that a smaller amount of silver solution might be used, and the bromine obtained more concentrated; but I have convinced myself by numerous experiments that it is requisite not to precipitate too little chloride of silver nor to use a hot solution.

I have been able to determine the bromine accurately according to this method in the mother-liquors from the salt works, and have obtained results which agreed with the estimation of the bromine from the colour of the ætherial solution.—*Journ. für Prakt. Chem.*, vol. xlv. p. 269.

PROCEEDINGS OF SOCIETIES.

Royal Society.

Nov. 23, 1848.

"On the Chemical Nature of Wax."—Part III. "On Myricine." By B. C. Brodie, Esq.

This paper is the last of three papers on the chemical nature of wax*, and contains the investigation of that portion of bees-wax which is soluble only with difficulty in boiling alcohol. This body could never be rightly investigated before the discovery of the true nature of the other constituent of the wax, namely, the cerotic acid, for the absence of which no test was known, and the products of the decomposition of which would materially interfere with any experiments on the nature of the myricine. When the cerotic acid has been absolutely removed by repeated boiling of the wax with alcohol, a substance remains, which is saponifiable, but with difficulty. From the products of saponification the author isolated palmitic acid, $C_{32}H_{32}O_4$, and a new wax-alcohol, analogous to, but yet different from cerotine, described in a former paper. This alcohol, melissine, has the formula $C_{60}H_{62}O_4$. By oxidation of this substance by means of lime and potash, the acid $C_{60}H_{60}O$, melissic acid, was obtained; and by the action of chlorine, a body analogous to chloral, a substance, that is, of the aldehyde series, but with a substitution of between fourteen and fifteen equivalents of chlorine for hydrogen. In its conversion into this substance the alcohol loses two equivalents of hydrogen, without substitution. The author also investigated the products of the distillation of myricine. From these he procured likewise palmitic acid and a solid hydrocarbon, which, rectified over potassium, had a melting-point of 62°, and contained, as shown by analysis, carbon and hydrogen in *equal* equivalents. The analogy of the mode of formation of this substance to cerotine from Chinese wax shows that it is the hydrocarbon, melene, $C_{60}H_{60}$. By repeated crystallization from ether a substance was obtained from the impure myricine, of a crystalline character, melting at 72°; the analysis of which agrees with the formula $C_{92}H_{92}O_4$, which explains the reactions of the substance.

* An abstract of the two former papers appeared in vol. vi. p. 225 of this Journal.

The general conclusion from this investigation is, that waxes are a class of bodies which, chemically speaking, stand in the same relation to fat as fatty bodies do to the alcohol and acetic acid of vinous fermentation; all which bodies are members of one chemical series, possess an analogous chemical character, and are susceptible of analogous transformations.

PATENTS.

Patent granted to Charles Low, Dalston, Middlesex, *for Improvements in manufacturing Copper.*

It is well known that in manufacturing copper from its ores, the ores are roasted, and then melted in a suitable furnace, and again roasted and again melted, until the process is finished. Now I have discovered that if a compound of oxide of manganese, plumbago, nitrate of potash, soda, or lime and carbon, be in the furnace when the melted matters are in the progress of their manufacture into copper, the time of bringing about the desired result is reduced, the slag so obtained contains less copper, and a saving of fuel is effected. The manner in which I prefer to carry on my invention is as follows:—I well mix the four ingredients above mentioned, in the state of powder or otherwise, in the following proportions:—oxide of manganese (black oxide of commerce), 42 parts; plumbago, 8 parts; nitrate of potash (or it may be nitrate of soda or lime), 2 parts; and of carbon (preferring anthracite coal or wood charcoal), 14 parts. On the first melting of the ores, and when the whole charge of a furnace is completely melted, for every ton of the charge I take 25 lbs. of the above mixture or combination, and throw the same on to the melted matters, and cause the whole to be well worked or rabbled, and it will be found that the process is materially quickened, the combination of materials acting as a flux in separating the metal, and the slag will rise to the surface more fluid and contain less copper than is usually the case. The slag is to be skimmed off, and another 25 lbs. of the combination or mixture is to be applied as before, and the mass under process well rabbled, and the slag again skimmed off, when a further quantity of the mixture or combination of materials above-mentioned is to be added, and the working conducted as above explained, and so on, till the workman, judging as heretofore, considers the metal to have arrived at a sufficiently forward state, when he will run off the charge and carry it through its subsequent process, as when working according to the ordinary means of making copper. But in some ores the metal will not be brought so forward by the first melting as with other ores, in which cases in the next melting the employment of the combination or mixture above-mentioned is again to be used. And I would state, that although I have described the use of my invention, to com-

mence with the first process of melting the ore, I do not confine myself thereto; I however believe that to be the best means of carrying my invention into practice; but whether the process be resorted to in the first or other meltings, the process will be advanced and benefited; and I believe in most cases the copper produced will be found of better quality than when made according to the ordinary process of manufacturing copper from copper ores.—Sealed Nov. 4, 1847.

Patent granted to Felix H. F. Louis, *for an improved method of preserving Milk.*

This invention consists in preserving milk by converting it into solid cakes or masses, which are soluble in warm water, and may be kept for a long time without losing their original sweetness and freshness. The milk in its natural state is mixed with well-clarified raw sugar in the proportion of 4 oz. of sugar to each gallon of milk, and it is then agitated and evaporated in pans by steam. When it approaches to a solid state, it is removed from the pans, and pressed in moulds into cakes of any suitable shape.

When great despatch is not requisite, the patentee employs a number of shallow pans, into which the milk (sweetened as before mentioned) is introduced to the depth of one-tenth of an inch, and left exposed to the atmosphere until it evaporates to dryness; the solid residuum is then collected and pressed into moulds. If the atmosphere is not in a sufficiently dry state for the operation, the pans may be placed in a drying chamber, kept at a temperature not exceeding 50° C. (122° F.)

Milk cakes of a very rich quality are produced by the following process:—The sweetened milk is heated nearly to the boiling-point, and allowed to cool slowly; when it comes to a tepid state, it is curdled by means of rennet or any weak acid, and then the whole is thrown into a sieve to separate the curd from the whey. The curd is washed with cold water, and then subjected to strong pressure, in order to free it from any water which it may contain; and the whey is evaporated to dryness in order to recover the salts with which it is charged. The curd is now placed in a pan over a slow fire, and stirred continually; and the salts recovered from the whey are gradually introduced, in small quantities at a time, accompanied by a small portion of bicarbonate of soda or some other alkali, say 1 part of alkali to 20 parts of the whey salts. After a time the contents of the pan begin to melt and amalgamate; and, while in this state, a small quantity of gum-dragon, finely pulverized, may be added, in order to facilitate the solidification of the mass.

Cream may be solidified as well as milk by any of the processes above described.—Sealed May 26, 1848.

THE CHEMICAL GAZETTE.

No. CLI.—February 1, 1849.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Investigation of Ox-bile. *By* A. Strecker.

This communication, which is in continuation of the author's researches published at p. 149 of our last volume, further confirms the view supported by Demarçay, Liebig, Theyer and Schlosser respecting the constitution of bile, according to which it must be looked upon as a soda salt of an organic substance of acid nature, and not as an indifferent organic body, which is converted into acids, ammonia and taurine by decomposition.

The author now shows by further experiments that this organic substance, as was indicated in his former paper, is not a single acid, but a mixture of a nitrogenous acid free from sulphur (*cholic acid*), which is precipitated by neutral acetate of lead, and a second acid containing both sulphur and nitrogen (*choleic acid*), which, after precipitation of the first, may be combined with basic acetate of lead; and that bile purified from fat, &c. contains no other constituents besides the salts of cholic and choleic acids, of which the bases are principally soda and variable quantities of magnesia, potash and ammonia. The assumption that bile in a fresh state consists of a single substance, which is only separated by decomposition into several acids—fellinic, cholinic, bilifellinic and bilicholinic acids—is declared by Strecker to be erroneous; on the contrary, a single acid may be obtained from the two principal constituents of the bile, both by decomposition with acids as well as with bases.

Cholic acid has already been sufficiently described by the author in his former paper; in the following, some new facts are brought forward, relating to the properties of the salts and the products of decomposition of this acid, which throw considerable light upon its composition. Under the influence of alkalies, cholic acid is resolved into glycocoll and *cholalic acid* (Demarçay's cholic acid); under the influence of acids it passes through some intermediate products, which at first appear to consist of bodies having the composition of cholic acid minus water, into glycocoll and Demarçay's choloidic acid. Choloidic acid itself is converted by long boiling with muriatic acid into the dyslysine of Berzelius. Cholalic acid, when boiled with strong muriatic acid, likewise passes into choloidic acid, and finally into dyslysine. The same products make their appearance when cholalic acid is exposed to an elevated temperature; it is first con-

verted, with loss of water, into choloidic acid; and at a still higher temperature, with a still further loss of water, into dyslysine.

With respect to the sulphuretted nitrogenous acid, which is called choleic acid, the author has only been able to determine its nature from its products of decomposition, as the acid itself is very unstable. It has a similar constitution to cholic acid, the latter being a conjugate compound of cholalic acid with glycocoll, while choleic acid is a conjugate compound of cholalic acid with taurine.

Products of Decomposition of Cholic Acid.—When the solution of a cholate is mixed with a solution of caustic potash until no more cholate of potash separates, the concentrated ley deposits on boiling an amorphous potash salt, which, on replacing the evaporated water and boiling from twenty-four to thirty-six hours, becomes crystalline. From the solution of this salt in water muriatic acid separates cholalic acid. The nitrogen of the cholic acid is contained in the substance dissolved in the alkaline liquid separated from the cholalate of potash; and this substance is sugar of gelatine or glycocoll.

It is however more advantageous to decompose the cholic acid with baryta instead of with potash, as the excess of the alkaline earth, after the cholalate of baryta and excess of hydrate of baryta have separated on cooling, may easily be removed from the liquid by means of carbonic acid, when the glycocoll can be detected in it. But as some cholalate of baryta remains in the solution, it is necessary to separate from the solution filtered from the carbonate of baryta the cholalic acid by the addition of muriatic acid, which is insoluble in water; the solution then contains only glycocoll and chloride of barium. The baryta is removed by sulphuric acid; and by subsequently boiling the liquid filtered from it with hydrated oxide of lead, the muriatic and sulphuric acids are eliminated; the solution now contains much lead; the lead is removed with sulphuretted hydrogen and the liquid evaporated. It furnishes crystallized glycocoll.

Thus the entire process of decomposition of cholic acid by alkalies consists in resolving it into cholalic acid and glycocoll. The minute traces of other substances which are generated, viz. ammonia and a volatile oily body of disagreeable odour, are secondary products of decomposition of glycocoll. Several grammes of pure glycocoll, boiled uninterruptedly for three days with concentrated solution of hydrate of baryta, furnished a distillate which contained ammonia and the same disagreeable substance, but both only in small quantity; for 2 drops of concentrated sulphuric acid served to neutralize the ammonia completely. The glycocoll reobtained after removal of the baryta had not diminished in appearance, and contained a mere trace of a crystalline substance soluble in æther.

Cholalic Acid, $C^{48}H^{40}O^{10}$ (with various amounts of water).—The cholalic acid, precipitated from its baryta or potash salt by means of muriatic acid, is at first resinous; it is left in the liquid until it has become solid and friable, which may be accelerated by the addition of a few drops of æther; it is then brought upon a filter, washed with cold water, and dissolved in boiling alcohol, from

which it crystallizes on cooling. In case the crystals should be coloured, it is best to reduce them to powder, and digest them with a little æther, which principally dissolves the colouring substance.

The crystals obtained in this manner, in general tetrahedrons and rarely octahedrons, are colourless, have a vitreous lustre, and are very brittle. In dry air their surface soon becomes opalescent, and the crystals become opake, with loss of water. They have a somewhat bitter taste, with a slight sweet after-taste; they require 750 parts boiling water and 4000 parts cold water for solution. In boiling alcohol they dissolve in considerable quantity, and on cooling a portion again separates in crystals; when the solutions are not perfectly saturated, the crystallization does not begin for several hours, and then proceeds very slowly. 1000 parts of cold alcohol of 0·889 spec. grav. retain 48 parts of dry cholalic acid in solution. The alcoholic solution is rendered turbid by the addition of water; and when set aside, acicular crystals, with very considerable lustre, generally separate, mixed with tetrahedrons. 1 part by weight of cholalic acid requires 27 parts of æther for solution. The ætherial solution, which is obtained by agitating æther with cholalic acid recently precipitated from the alkaline solution, deposits on spontaneous evaporation colourless transparent crystals, which do not effloresce in dry air. The acid crystallized from ætherial solutions, $C^{48}H^{41}O^{11}+HO$, forms right rhombic prisms. The crystals which separate from a boiling alcoholic solution on cooling, $C^{48}H^{40}O^{10}+5HO$, belong on the contrary to the quadratic system.

The acid crystallized in tetrahedrons or square octahedrons parts very slowly, but entirely, with the whole water of crystallization (of which the quadratic crystals contain 9·9 per cent. = 5 atoms) when dried at 212°. No further loss occurred when they were subsequently heated up to 302°; their form is not changed, but they become opake and white. The analysis of the acid dried at 212° gave—

Carbon	70·54	70·49	69·91	48 =	288	70·59
Hydrogen ..	9·84	9·90	9·70	40	40	9·80
Oxygen	19·62	19·61	20·39	10	80	19·61

The acid which crystallizes in rhombic prisms contains in the air-dried state 2 atoms of water of crystallization, of which only 1 atom is expelled at 212°:—

	Air-dried acid.			Acid dried at 212° F.				
Carbon	68·3	48	67·6	68·7	69·2	69·0	48	69·1
Hydrogen	10·0	42	9·9	9·8	9·9	9·8	41	9·8
Oxygen	21·7	12	22·5	21·5	20·9	21·2	11	21·1

Once, when the rhombic crystals had been dried at 212° for fourteen days, they yielded the composition of the acid $C^{48}H^{40}O^{10}$.

Lastly, the acid which separates from alcohol in needles exhibits, upon the addition of water, some further differences from the two preceding modifications. At 212° it lost 2·4, and at 284° 4·8 per

cent. of water. When heated more strongly, to 293°, the acid fused partially and acquired a yellow colour. According to this the formula of this acid appears to be $C^{48}H^{40}O^{10} + 2HO$; at 212° 1 atom of water = 2·1 per cent. escapes, and at 248° the acid loses both atoms of water = 4·2 per cent.

These three different forms of cholalic acid are nothing more than modifications of one and the same acid; they probably correspond to its three different origins from cholic acid, paracholic acid and amorphous cholic acid, for the salts prepared from the several modifications exhibit no difference in their properties and composition; and, moreover, by employing a different solvent and careful attention to the proportions, either of the modifications may be converted into the other.

The Salts of Cholalic Acid, $C^{48}H^{39}O^{9}, MO$, have in general a very bitter taste, which is at the same time somewhat sweetish, and are all of them soluble in alcohol. When heated with concentrated sulphuric acid and solution of sugar, they exhibit the same violet colouring as the salts of cholic acid. Cholalic acid is dissolved by dilute solutions of caustic potash, soda and ammonia in considerable quantity. In solutions of the alkaline carbonates it dissolves on the application of heat, with disengagement of carbonic acid. On evaporating the neutral solution by heat, the cholalate separates in a crystalline state, whilst on spontaneous evaporation it is left as an amorphous residue with a varnish lustre. The salt dissolves readily in alcohol, and separates in a crystalline state on evaporating the solution. An aqueous solution of cholalate of potash, containing about 3 per cent. of cholalic acid, exhibits the following reactions:— With chloride of barium no precipitate (except in concentrated solutions of cholalic acid, when a flocculent precipitate is produced); with chloride of calcium the whole liquid becomes thick like paste, and upon the addition of a few drops of æther, acicular crystals are formed in the liquid after some time; with acetate of copper, an abundant bluish-white precipitate; with protoxide of manganese, a flocculent semi-crystalline precipitate; with perchloride of mercury, a white precipitate, which dissolves partially on boiling; the same with a solution of the protoxide of mercury; and with nitrate of silver a bulky white precipitate, which is likewise partly dissolved on boiling the liquid without becoming black.

Cholalate of Potash, $KO, C^{48}H^{39}O^{9}$ (dried between 212° and 300°), is obtained by neutralizing an alcoholic solution of cholalic acid with potash and mixing it with æther, when the salt very soon separates in needles. It is also obtained in minute crystals on evaporating the alcoholic solution. The salt, dried at 212°, may be exposed to 300° without experiencing the slightest change. When heated more strongly, it melts, and finally burns with considerable tumescence. Dried within that temperature, it gave on analysis,—

Carbon.....	63·98	63·90	48 =	288	64·56
Hydrogen.....	8·79	8·73	39	39	8·74
Oxygen	16·05	16·85	9	72	16·14
Potash	11·18	10·52	1	47·1	10·56

Cholalate of Soda is exactly similar to the potash salt.

Cholalate of Ammonia is obtained when ammoniacal gas is passed into an alcoholic solution of cholalic acid and æther added, upon which prismatic or acicular crystals separate. When their aqueous solution is boiled, ammonia escapes; after some time it becomes turbid, and on evaporation leaves a resinous mass, which now merely contains a trace of ammonia and has an acid reaction. It also parts with ammonia after long exposure to the air, and consequently behaves perfectly similar to the cholate of ammonia.

Cholalate of Baryta, $BaO, C^{48} H^{39} O^{9}$ (dried at 212°).—Cholalic acid is very soluble in barytic water. If the excess of baryta is precipitated by carbonic acid, the solution then slowly heated to boiling, filtered from the carbonate of baryta, and evaporated, as the water escapes it becomes covered with a crystalline pellicle of pure cholalate of baryta of silky lustre on the under side, and covered with warty excrescences above. It dissolves in 30 parts of cold and 23 parts of boiling water; it is far more soluble in alcohol, and is left on evaporation as a crystalline crust.

When carbonic acid is passed into the aqueous solution of this salt, after some time carbonate of baryta and the acid subside from the solution; the latter may be separated from the baryta by alcohol or æther, in which it dissolves, which shows that the precipitate is not a bicholalate of baryta. When the liquid is heated with the precipitate, the latter disappears almost entirely; but the liquid does not become perfectly clear, a portion of the cholalic acid remaining undissolved. From the alcoholic solution of the baryta salt carbonic acid separates nearly the whole amount of baryta. The salt, dried at 212°, gave—

Carbon	60·25	59·94	60·02	..	48	288	60·58
Hydrogen	8·32	8·21	8·24	..	39	39	8·20
Oxygen	..	..	..	..	9	72	15·15
Baryta	15·94	16·20	16·07	16·04	1	76·4	16·07

Cholalate of Lime, $CaO, C^{48} H^{39} O^{9}$ (dried at 212°).—The aqueous solution of the cholalate of baryta yields with chloride of calcium a thick curdy precipitate, which crystallizes on the addition of æther, and may then be easily washed. This salt is very sparingly soluble in cold water, much more so in hot. It afforded 6·64 per cent. of lime; the formula requires 6·56 per cent.

Cholalate of Silver.—A solution of cholalate of baryta in 100 parts of water still furnishes a considerable precipitate with nitrate of silver, which partially dissolves on boiling, and again separates on cooling in a crystalline state. When the aqueous solution of the silver salt is mixed with a little acetic acid, it becomes turbid; and after some time minute traces of crystallized cholalic acid separate. The salt gradually becomes black at 212°. It dissolves readily in alcohol.

Constitution of Cholic Acid.—What has been stated above will serve to establish the composition of cholalic acid; and it has been observed in the commencement, that, in the conversion of cholic

acid into cholalic acid, glycocoll (which was proved to be such from its properties and analogies) separates ;—it now therefore remains to deduce from these products of decomposition the constitution of cholic acid (cholic acid = $C^{52}H^{43}NO^{12}$, cholalic acid = $C^{48}H^{40}O^{10}$, and glycocoll = $C^4H^5NO^4$). Now

$$C^{48}H^{40}O^{10} + C^4H^5NO^4 - 2HO = C^{52}H^{43}NO^{12},$$

which equation shows that the constitution of cholic acid is perfectly analogous to that of hippuric acid, 1 atom of benzoic acid + 1 atom glycocoll — 2 atoms water expressing the composition of hippuric acid.

Products of Decomposition of Cholic Acid by Acids: Choloidic Acid, Dyslysine and Glycocoll.—Cholic acid dissolves readily in cold concentrated muriatic and sulphuric acids, and is again separated unaltered upon the addition of water. But if the solution is heated to boiling, it soon becomes turbid, and oily drops separate, which harden and become resinous as the liquid cools. If the liquid is poured off from the separated substance and evaporated, a very small residue is left, which consists, when muriatic acid has been employed, of a resinous substance and traces of muriate of glycocoll. Since, consequently, no other products appear besides the body eliminated on boiling, and this has not absorbed any muriatic acid, it can only differ from cholic acid in the amount of water. This substance possesses the character of a weak acid ; it dissolves in ammonia and in the fixed alkalies, and its solution is precipitated by salts of baryta and lime in thick flakes. The ammoniacal solution is moreover precipitated by carbonate of ammonia, chloride of ammonium, and many other saline solutions; so that this acid closely resembles hyocholic acid. But the salt of ammonia does not separate in crystalline flakes on the addition of a solution of chloride of ammonium like the hyocholate of ammonia, but as a viscid mass.

When the resinous mass is dried in the water-bath, it melts on longer exposure, gradually hardens, and on cooling is perfectly brittle. Nevertheless it cannot be dried at this temperature, for after more than eight days' exposure in the water-bath it still decreased in weight. But if the substance is dried at 284°, at which temperature it is at first liquid but after some time merely soft, it no longer dissolves in cold ammonia. Upon the addition of some æther containing alcohol, it cakes together without much being dissolved.

This substance possesses the characters of a weak acid ; the abovementioned baryta precipitates contain but small and variable quantities of baryta. It is to be considered as an intermediate product in the decomposition of cholic acid by acids, and possesses no characters by which its purity can be ascertained. The determinations however of the carbon and water, and the circumstance that no nitrogen and no carbon separate in this treatment, show that the change of cholic acid in the first action of muriatic acid upon it consists in its losing 2 to 4 atoms of water.

When, on the other hand, cholic acid is dissolved in water, and the boiling continued after the resinous substance has separated, further decomposition occurs. The liquid resin, which at first was

like an oil, becomes gradually more solid, and at last no longer melts in the boiling liquid. If it is analysed from time to time, a constant increase of the carbon is observed until it amounts to about 77 per cent., when no further change takes place. At the same time the solubility in alcohol diminishes, and the final product is insoluble in cold and but sparingly soluble in boiling alcohol; the solubility in æther, on the contrary, increases, the final product being readily soluble in æther. This substance has all the properties of the dyslysine of Berzelius. Before, however, this final product made its appearance, a well-characterized acid separated as intermediate product, viz. Demarçay's

Choloidic Acid, $C^{48}H^{39}O^{9}$ (dried at 212°).—This acid combines with bases without elimination of basic water; it is white in the pure state, readily reduced to powder, insoluble in hot water and fusible; when it has been dried, it melts at a temperature of about 302°, previously passing through different degrees of softness. It dissolves readily in alcohol; an addition of water renders the solution turbid, and when set aside the acid separates as a resinous mass. The supernatant liquid continues turbid for a very long time, and it may be evaporated at a gentle heat to half its volume without becoming clear. The alcoholic solution has an acid reaction. Choloidic acid is very sparingly soluble in æther; it is therefore best purified by solution in alcohol and precipitation with æther, re-solution in alcohol and precipitation with water.

Choloidic acid combines with bases, and expels carbonic acid from solutions of the alkaline carbonates on the application of heat. The alkaline salts are soluble in water and in alcohol, but insoluble in æther. The weakest acids, even a current of carbonic acid, separate choloidic acid from the aqueous solution of these salts. These salts have a purely bitter taste, without any sweet after-taste, as is the case with the cholates. The soluble salts are obtained on evaporating the aqueous or alcoholic solutions as gummy masses. The acid dissolves entirely in solution of ammonia; but on boiling the solution, ammonia gradually escapes, so that after a time it has an acid reaction. With the earths and oxides of the heavy metals choloidic acid forms salts, which are insoluble or very sparingly soluble in water, but all dissolve in alcohol. They are obtained by precipitating an alkaline choloidate with the corresponding metallic solution, generally in the form of adhesive, plaster-like precipitates. The analysis of the acid, dried at 212°, gave—

Carbon.....	71·92	71·98	48 =	288	72·18
Hydrogen	9·78	9·80	39	39	9·77
Oxygen	18·30	18·22	9	72	18·05

The atomic relations adopted are confirmed by the composition of the following salt:—

Choloidate of Baryta, $BaO, C^{48}H^{39}O^{9}$ (dried at 212°), has the same composition as the cholalate of baryta, but very different properties. The baryta salt of choloidic acid is almost insoluble in water and amorphous; that of cholalic acid is soluble and crystalline.

In this respect cholalic acid stands to choloidic acid in the same relation as camphoric acid to anhydrous camphoric acid, which acids also form salts possessing the same composition but essentially different properties. This salt was obtained by mixing an excess of barytic water with an alcoholic solution of choloidic acid, evaporating to dryness, and treating the residue with cold alcohol; the solution was evaporated, the residue dried at 248° and analysed; it gave—

Carbon.....	60·40	48 =	288	60·58
Hydrogen.....	8·32	39	39	8·20
Oxygen.....	15·21	9	72	15·15
Baryta	16·07	1	76·4	16·07

Glycocoll.—On treating cholic acid with acids, the liquid from which the choloidic acid has separated is found to contain muriate of glycocoll. It is evaporated to dryness, the residue dissolved in water, and the filtered solution boiled with hydrated oxide of lead; the whole of the muriatic acid is separated in this manner, but a considerable quantity of oxide of lead dissolved; this is precipitated with sulphuretted hydrogen, when the colourless solution deposits on concentration prismatic crystals of glycocoll.

Previous to the metamorphosis of the choloidic acid into dyslysine, and when the decomposition of the cholic acid consequently consists merely in a separation into choloidic acid and glycocoll, this metamorphosis may be expressed by the following equation:—

$$C^{48}H^{39}O^{9} + C^{4}H^{5}NO^{4} - HO = C^{52}H^{43}NO^{12}.$$

Products of the Action of Muriatic Acid upon Choloidic Acid: Dyslysine, $C^{48}H^{36}O^{6}$ (dried at 248°).—By long-continued boiling of choloidic acid with strong muriatic acid, its properties gradually disappear, and it finally changes into the substance called dyslysine by Berzelius. The choloidic acid, which at first melts like a resin, no longer fuses, and has a very brown colour. The pulverized resinous substance is first exhausted with water, then with boiling alcohol, and finally dissolved in æther. Upon the addition of alcohol to this solution, the dyslysine is separated in the state of a powder, and forms when dry a grayish-white mass. It then possesses the following properties:—It is insoluble in water and cold alcohol, sparingly soluble in boiling alcohol, soluble in æther; it is not dissolved by ammonia or solution of potash; by boiling with an alcoholic solution of potash, or after fusion with hydrate of potash, it dissolves; but on the addition of acids to this solution, a resinous body separates, which is no longer dyslysine, but identical with choloidic acid. According to the observations of Berzelius, a small quantity of cholalic acid (cholic acid of Berzelius) is formed at the same time.

The origin of dyslysine from choloidic acid, and its re-conversion into the same, satisfactorily show that dyslysine contains 48 atoms of carbon. Analysis gave the following numbers:—

Carbon	77·6	77·3	48 =	288	77·4
Hydrogen	9·6	9·6	36	36	9·6
Oxygen	12·8	13·1	6	48	13·0

If we compare the composition of choloidic acid with that of dyslysine, we find that on the conversion of the former into dyslysine 3 atoms of water are eliminated, and on the conversion of the latter into choloidic acid 3 atoms of water absorbed.

Products of the Action of Muriatic Acid and a high Temperature upon Cholalic Acid: Choloidic Acid and Dyslysine.—The cholalic acid in tetrahedrons, dried at 212°, may be heated to 302° and above, without loss of weight. At 383° it melts, with loss of 2·2 to 2·4 per cent. water, and forms a resinous substance possessing all the properties of choloidic acid. The formulæ of the acids require the elimination of 1 atom of water = 2·2 per cent. If the mass, fused at 390°, is heated still further up to 554° (it does not become brown before 572°), the acid, dried at 365°, loses 7·3 per cent., and has now the properties of dyslysine. The formulæ of these two substances require for this the elimination of 4 atoms of water. We have—

In the first case .... $C^{48} H^{40} O^{10} - C^{48} H^{39} O^{9} = HO$.
In the second ..... $C^{48} H^{40} O^{10} - C^{48} H^{36} O^{6} = 4HO$.

If cholalic acid is boiled for some time with strong muriatic acid, it is converted into a resinous body, which no longer separates in a crystalline state from the alcoholic solution upon the addition of water, but amorphous and transparent. This substance is choloidic acid. If the boiling is continued longer, the final product is found to be dyslysine.

Upon again taking into consideration the behaviour of cholic acid towards strong acids, we might be led to suspect that at first it would simply separate into glycocoll and cholalic acid; and that the subsequent products would originate from the further metamorphoses of the cholalic acid, which by the prolonged action of muriatic acid would be converted into choloidic acid and dyslysine. However, the decomposition does not take place in this manner, as is proved by the analyses of the nitrogenous intermediate products, and the negative results obtained on examining the resin which separated at the commencement for the presence of cholalic acid. In the action of strong acids and alkalies upon cholic acid, it separates therefore into glycocoll and a non-nitrogenous substance; with alkalies only a single acid is constantly produced, cholalic acid; but with acids the product obtained possesses, according to the length of the treatment, different properties and composition; at first it is a weak acid, whilst the final product is a perfectly neutral substance.

[To be continued.]

On an Organic Compound containing Arsenic obtained in the Distillation of Butyrate of Potash and Arsenious Acid. By Prof. Wöhler.

In the distillation of a dry mixture of equal parts by weight of butyrate of potash and arsenious acid, a product was obtained consisting of two liquids, the upper one acid and almost colourless, the

under one coloured nearly black by metallic arsenic and possessing the same odour as oxide of cacodyle: at the same time a considerable quantity of a very fœtid gas was given off, and much arsenic was reduced. When the product, after it had been shaken with magnesia and water, was again distilled, a heavy, oily, colourless substance passed over with the water, which, when it came into contact with the atmosphere, became orange-coloured, and finally dark brown. This substance had a most disgusting cacodylic odour, burnt with a white flame, giving off arsenical fumes, but did not spontaneously ignite nor fume in the air. On digestion with concentrated muriatic acid, the odour became extremely irritating to the nose and eyes.

The aqueous liquid which distilled over with it, and which appeared to contain a large quantity of the oil in solution, furnished a bulky nearly-white precipitate with a solution of perchloride of mercury; and the odour of cacodyle disappeared almost entirely, to make place for an aromatic odour resembling that of butyrone. The precipitate dissolved on being heated, and separated on cooling in minute crystals. When the liquid, together with the crystalline deposit, was mixed with muriatic acid and zinc shavings, the nauseous odour of cacodyle very soon made its appearance again; and the hydrogen disengaged diffused dense white vapours in the air, and deposited an orange-coloured substance upon a flask against which it was directed. On distilling the mixture, a colourless oily substance, of a most disagreeable odour, passed over, fumed in the air, but did not ignite spontaneously.

It should be observed that the butyrate of potash employed in this experiment had been prepared by decomposing butyric æther with an alcoholic solution of potash, after the æther had been previously heated nearly to boiling for several hours in a suitable vessel, in order to remove every trace of acetic æther, should any be present.

This experiment shows, that in the distillation of butyrate of potash with arsenious acid, either an analogous compound to cacodyle or the oxide of cacodyle is formed, or that these are generated, and are only modified in their properties by an admixture of other products. Prof. Wöhler states that it is not his intention of following up this subject any further.—Liebig's *Annalen*, October 1848, p. 127.

New Substance occurring in the Urine of a Patient with Mollities Ossium. *By* Dr. Bence Jones.

The urine in this case spontaneously solidified on cooling, but was reliquefied by heat. The substance to which this property was due constituted as much as 67 parts per 1000 of the urine. It was quite insoluble in alcohol, and was completely precipitated from the urine by the addition of that reagent. It slowly but entirely dissolved when thrown into cold water, but was much more readily dissolved by boiling water. After boiling for some time, a gelatinous coagulation took place. The aqueous solution gave an imme-

diate precipitate with nitric acid, which entirely and readily dissolved when heated. Boiling caused no precipitation, but on cooling the precipitate was again formed. Strong hydrochloric acid dissolved the substance, giving a splendid purple-blue solution. It was soluble in caustic potash at 140°, or after long standing at the ordinary temperature. From this solution it could be precipitated by excess of acetic acid, but the precipitate was redissolved as before by heat. When the alkaline solution was boiled, a deep inky blackness was produced by dropping acetate of lead into the solution. If the aqueous solution was acidulated with acetic acid, an immediate white precipitate fell on the addition of ferrocyanide of potassium.

These reactions announce the substance in question as completely *sui generis*. From ultimate analysis its composition per cent. was found to be,—C, 52·10; H, 6·70; N, 15·17; O, 26·00; with 1·03 per cent. sulphur and 0·19 phosphorus.

The presence of sulphur and phosphorus in this new substance proves that it is not an oxide of proteine. The solubility of this body in water might lead to the comparison of it with the hydrated tritoxide of proteine of Mulder, which is also soluble in water; but according to Mulder, this hydrated tritoxide of proteine gives no precipitate on the addition of ferroprussiate of potash, and it contains no sulphur or phosphorus, while this new substance gives both sulphur and phosphorus, and also a precipitate with ferroprussiate of potash. In these respects there is a most marked and essential difference between these substances. The peculiar reaction of this new body with nitric acid, the solubility of the nitric acid precipitate when heated, I find to be also common to the so-called hydrated tritoxide of proteine prepared from the inflammatory crust of the blood; from albumen of the blood by chlorine; and from albumen of the egg. Lastly, this peculiar reaction with nitric acid hinders all possibility of confusing this new substance with albumen. Indeed ordinary albumen may be separated from this new substance by adding nitric acid, boiling and filtering whilst hot; on cooling, the hydrated oxide will be precipitated from the filtered liquid, and it will again be redissolved by heat, whilst the albumen will remain on the filter.—*Phil. Trans.*, 1848, part 1.

On some Combinations of Phosphoric and Pyrophosphoric Acids. *By* W. Baer.

The author first analysed the ordinary phosphate of lime, which he obtained in a crystalline state by precipitating with chloride of calcium a solution of ordinary phosphate of soda, rendered strongly acid with acetic acid. It had the following composition:—

$$\left.\begin{matrix}2CaO\\HO\end{matrix}\right\} PO^5 + 4HO.$$

The water which this salt contains is partly expelled at 302°, but it requires a red heat to drive it all off.

When pyrophosphate of soda is precipitated with chloride of cal-

cium, the voluminous deposit dissolves, although with difficulty, in acetic acid; and after some time crystals of the pyrophosphate of lime separate from the solution. It may also be obtained immediately in the crystalline state by precipitating with an excess of chloride of calcium a solution of pyrophosphate of soda acidified with acetic acid. The composition of this salt is represented by the formula $2CaO, PO^5 + 4HO$.

If, in the preparation of the preceding salt, the pyrophosphate of soda is allowed to predominate, the precipitate always contains some soda. A well-defined double salt may be obtained by digesting the precipitate of pyrophosphate of lime for some time in the mother-liquor, containing an excess of pyrophosphate of soda. This crystalline salt is represented by the formula

$$\left.\begin{matrix}CaO\\NaO\end{matrix}\right\} PO^5 + 4HO.$$

When pyrophosphate of soda is precipitated with a solution of barytic water, strontia, magnesia, and even silver, always allowing the alkaline salt to be in excess, the precipitates obtained contain soda; but it seems impossible to procure well-defined compounds. They are probably mixtures of a double salt with a simple and insoluble pyrophosphate, as the somewhat complicated formulæ which the author has deduced from his analyses would seem to show.—Poggendorff's *Annalen*, lxxv. p. 319.

On a new Compound of Boracic Acid with Soda, and on the probable mode of formation of Boracic Acid. By Dr. P. Bolley.

I was led to this inquiry from having frequently observed that, on mixing solutions of borax and chloride of ammonium, ammoniacal gas is disengaged. This fact, of which I could find no mention in any work, probably from its apparent unimportance, may be explained in two ways; either an exchange of bases and acids may take place, and borate of ammonia and chloride of sodium be formed from borate of soda and chloride of ammonium, and the borate of ammonia parts with ammonia even at a low temperature like other ammoniacal salts (that it is decomposed at a high temperature, with elimination of ammonia, is well known); or the chlorine of the sal-ammoniac may deprive the borax of a part of its soda, forming a corresponding amount of chloride of sodium, ammonia being thereby liberated, while with the remainder of the soda a salt might be formed with a larger amount of boracic acid. It seemed to me worth the trouble to ascertain which of these suppositions was true; for if the latter happened, we might expect to obtain the long-missed quadriborate of soda on employing the two bodies in suitable proportions. The following are the salts of boracic acid with soda known at present:—NaO, BO^3; $NaO, 2BO^3$; $NaO, 6BO^3$. There are evidently some members missing in this series.

Chloride of ammonium was mixed with crystallized borax in the proportion of 2 equivs. of the latter to 1 of the former; the whole

dissolved and boiled as long as ammoniacal vapours were given off. The solution was then filtered and very gradually evaporated. This experiment was frequently repeated, but each time the same evil occurred, that the first crops of crystals were borax; and on further evaporation, if the temperature had been somewhat too high, the solution became syrupy and deposited no more crystals. But on very slow evaporation, some crystalline crusts separated at the bottom and on the surface, which agreed in their external characters and in their chemical reactions. After being rinsed with water and recrystallized once, they were obtained nearly free from chlorine; the mother-liquor always contained a large quantity of chloride of sodium. These crusts are very hard, milk-white or vitreous, shining, and presenting upon the surface an agglomerate of minute intimately-adherent crystals, but exhibiting on fracture a radiate structure. They contain much water, which escapes on the application of heat, without however puffing up so much as borax. The crystals dissolve in from 5 to 6 parts of water at the ordinary temperature. This solution furnishes, even with dilute sulphuric or nitric acid, white granular precipitates, consisting of boracic acid. This behaviour alone would prove that the mass was no mixture of borax with free boracic acid; for in a saturated solution of borax, made at the ordinary temperature, an addition of acid does not eliminate any boracic acid; on the contrary, the latter is more soluble in water to which some acid has been added than in pure water. The solution of the crystals has no action upon turmeric or litmus-paper; whilst an ordinary solution of borax, as also a solution of boracic acid, turns turmeric-paper quite brown.

The analysis of the salt, by decomposition in a platinum dish with recently-prepared hydrofluoric acid, addition of sulphuric acid, and determination of the sulphate of soda, gave the following results:—

Soda	17·60	17·35	16·44	1	18·23
Boracic acid	82·40	82·65	83·56	4	81·77

The amount of water which the powdered salt lost over sulphuric acid was 32·36, 34·0, 34·5, 34·99 per cent., which corresponds to—

	Calculated.	Found.
1 equiv. soda	11·92	11·50
4 equivs. boracic acid	53·46	53·88
10 equivs. water	34·61	34·61

The solution of the salt furnished precipitates with all those saline solutions with which a solution of borax yields precipitates; they do not differ in colour and solubility, and have also that in common, that on washing the precipitates furnished by heavy metallic oxides, the amount of boracic acid diminishes very considerably.

I shall now give my view respecting the formation of native boracic acid and of sassoline, which I consider to be very simple and in perfect conformity with nature. I explain the formation of boracic acid from the behaviour of borax towards chloride of ammonium.

Among recent chemists Payen has especially devoted attention to the formation of native boracic acid. As is well known, it has hitherto only been found in Tuscany, in the neighbourhood of Sienna, near Castelnuovo and Sasso, and on the island Volcano; in both places in a volcanic district, and at both localities accompanied with hot vapours, which rise from the earth. Payen explains the formation of the boracic acid by assuming that strata of sulphuret of boron occur at some depth, which are decomposed by the percolating water of the ocean, producing boracic acid and sulphuretted hydrogen. Part of the boracic acid sublimes, forms precipitates, and reaches the lagoons; part of it decomposes the salts contained in the sea water, and the carbonate of lime of the rock thereby liberating carbonic and muriatic acids, &c. This is one hypothesis founded upon another; it assumes the existence of a substance, sulphuret of boron, which has never been found hitherto; and the possibility of its being formed in nature, to judge of its artificial preparation, presupposes a rare coincidence of favourable conditions.

I have found that boracite and datolite, which are borates of magnesia and lime, behave precisely like borax towards chloride of ammonium, liberating ammonia. But there are several minerals besides these and tinkal which contain boracic acid, for instance tourmaline, axinite, &c. Now, in a volcanic district, where the occurrence of native sal-ammoniac is quite usual, it merely requires the presence of any such mineral, and the conditions requisite for the production of boracic acid are given. When an excess of chloride of ammonium is present, the borax is entirely decomposed into chloride of sodium and boracic acid; and the same is undoubtedly the case with the other compounds of boron. The ascent of the boracic acid with the hot vapours is readily explained, from the known property of this acid of being volatilized from aqueous or alcoholic solutions with the vapours of these liquids. The occurrence of ammonia, observed by Payen, in the vapours collected by him at Monte Rotundo in Tuscany, where native boracic acid occurs in such abundance, greatly favours the view that the boracic acid of the lagoons is formed in the manner above indicated.—Liebig's *Annalen*, October 1848, p. 122.

ANALYTICAL CHEMISTRY.

On the Estimation of Phosphoric Acid in Organic Compounds. *By* Prof. G. J. Mulder.

The quantitative determination of phosphorus in organic compounds is accompanied with more than one difficulty; the amount of the phosphorus is excessively small, and the form in which it occurs is often twofold. When, for instance, fibrine is dissolved in muriatic acid, and a solution of a weighed piece of iron and ammonia added, perphosphate of iron and peroxide of iron are obtained. If another quantity of fibrine is dissolved in nitric acid, and treated in the

same manner as the muriatic solution, the amount of phosphoric acid obtained is far greater; the reason of this is owing to the different states in which the phosphorus is contained in organic compounds.

In my investigations on the compounds of animal proteine I have always employed Berthier's method for determining the phosphorus. This method, as is well known, is not considered to be very accurate when the acid is contained in a substance in combination with lime; for if a weighed piece of iron be dissolved in nitric acid, and a muriatic solution of fibrine for instance added, ammonia precipitates everything which is not soluble in it; and among other things, sulphate of lime, if any is contained in the solution. Whilst the increase in weight of the iron employed, calculated as peroxide, may amount to more than is to be ascribed solely to the phosphoric acid, the increase in the second experiment, in which the nitric solution of the organic substance is mixed with the solution of iron and precipitated with ammonia, is not great enough to indicate the phosphoric acid by which the nitric solution had been increased.

When, for instance, phosphoric acid $+ a + b$ is precipitated from muriatic acid by peroxide of iron, the same phosphoric acid $+ a + b +$ the phosphoric acid produced by oxidation is obtained from nitric acid. Consequently two experiments are necessary, the one with muriatic the other with nitric acid; what the first experiment gives must be deducted from the result of the second; the remainder is the phosphoric acid formed by oxidation by the nitric acid. If no other compound of phosphorus is contained in the substance than phosphoric acid, the same result is obtained in both cases. With all its advantages, Berthier's method has this inconvenience, that it is not every kind of iron that furnishes the same amount of peroxide; it is therefore necessary to ascertain how much oxide the iron employed will yield. The iron which I have used of late gave 142·3 $Fe^2 O^3$. In substances which contain neither phosphorus nor phosphoric acid, as for instance vegetable gelatine or horn, we find that the nitric and the muriatic solutions give exactly the same result. Another example, which is in favour of Berthier's method, is that caseine constantly furnishes the same increase in weight of the iron, calculated as oxide, from a muriatic as from a nitric solution. The amount of phosphoric acid, calculated from the two precipitates, corresponds in both cases to 3·5 per cent. I will now mention a case in which the result furnished by the muriatic solution differs from that of the nitrate, for instance with albumen, where the muriatic solution gives 0·35 per cent. and the nitric solution 0·78 per cent. phosphorus; according to this experiment the compound contains 0·35 per cent. of phosphorus in the state of phosphoric acid, whilst 0·43 per cent. must have been oxidized by the nitric acid. In the same way albumen from blood gave 0·37 from the muriatic solution and 0·70 per cent. phosphorus from the nitric solution. The muriatic solution of fibrine gave 0·33 and the nitrate solution 0·66 per cent. phosphorus.

The difference is sufficiently distinct, and I can ascribe it to no other than the above cause that the phosphorus is contained in or-

ganic substances in different states; were we to suppose that the muriatic acid is not able to dissolve the whole of the phosphate of lime, or that it is not able to decompose completely a compound of phosphoric acid with organic substances, caseine furnishes an example to the contrary, as in this case muriatic acid and nitric acid give the same results. We must therefore distinguish in organic compounds the phosphoric acid existing as such from that which is produced by the action of the nitric acid.

That the phosphoric acid existing as such cannot be determined by burning the substances was shown some years ago by Baumhauer, as on burning vitelline 3 per cent. of phosphoric acid were volatilized. Vitelline, which on treatment with nitric acid furnishes 3 per cent. of phosphoric acid, leaves scarcely 0·3 of ash. 0·166 grm. calcined phosphoric acid, mixed in a porcelain crucible with 0·895 grm. lamp-black and heated to redness, left 0·109 residue. When there is not sufficient base present to combine with the phosphoric acid, its quantity can never be ascertained from the amount of ash.

Baumhauer employed a method of estimating the phosphoric acid by precipitation with peroxide of iron and ammonia, then dissolving the peroxide of iron in acetic acid, and weighing only the perphosphate of iron. If the perphosphate of iron were insoluble in acetic acid, this method would deserve recommendation; but such is by no means the case, as it is easily to be convinced of by adding ammonia to the persulphate, or pernitrate, or especially the perchloride of iron, and then acetic acid to redissolve the precipitate; when to the solution phosphoric acid is added in drops, a copious precipitate is produced; it disappears after some time, and is not perceptible upon a filter. Or when to a mixture of nitrate of iron and phosphoric acid ammonia is added, and then acetic acid, we shall always have a considerable loss, and when little iron is employed nothing upon the filter; Baumhauer's method therefore is unserviceable.

Fresenius's method of precipitating the phosphoric acid as ammonio-phosphate of magnesia, and calculating its amount from the pyrophosphate of magnesia, furnishes a very excellent means of estimating this acid; but it still remains to be ascertained whether this method is applicable in the investigation of organic substances containing phosphorus. The experiments I have made on this subject have furnished such discordant results, that I certainly cannot recommend it.

Norton obtained very good results by estimating the phosphoric acid as phosphate of baryta. By this means it is possible to determine the phosphorus and sulphur in the same quantity of the organic compound; but it has this disadvantage, that some carbonate of baryta is simultaneously precipitated by the ammonia, which may do no harm in mineral analyses, but in organic substances gives rise to serious errors. When chloride of barium is added to a solution of albuminous substances in muriatic or nitric acid, filtered, and ammonia added by degrees to the filtrate, phosphate of baryta is precipitated. After ignition this salt is $2BaO, PO^5$. With due precaution this method is as good as that of Berthier; but I recom-

mend the latter when the phosphoric acid occurs in small quantities, as in albuminous substances, or is produced in them by the oxidizing influence of nitric acid.—*Journ. für Prakt. Chem.*, xlv. p. 282.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Manufacture of Vitrifiable Pigments. By A. Wæchter*.

The art of painting with vitrifiable pigments has not kept pace with the progress of science, and is far from having attained that degree of perfection of which it is capable. It still presents too many difficulties to prove a fertile field to the artist for his labours; and its products have, for this reason, never held that rank in art which is due to them from the indestructibility and brilliancy of the colours. The reason of this is attributable to the circumstance that the production of good vitrifiable pigments is mere chance work; and, notwithstanding the numerous papers published on the subject, is still the secret of the few. The directions given in larger works and periodicals are very incomplete and indefinite; and even in the otherwise highly valuable 'Traité des Arts Céramiques' of Brongniart, the chapter on the preparation of colours is far from satisfactory, and is certainly no frank communication of the experience gathered in the royal manufactory of Sèvres.

Now it is equally important to art and science that as many persons as possible should contribute to develope this art; but so long as every individual about to engage in the subject finds himself compelled, as I was on commencing, to discover the knowledge already acquired by others, but kept secret, the cost of time and trouble requisite is sufficient to frighten most persons, and, what is of greatest injury to the art, especially the scientific chemist, from working on the subject.

The branch of painting with vitrifiable pigments which has acquired its greatest development is the art of painting on porcelain. The glaze of hard felspar porcelain, owing to its difficult fusion, produces less alteration upon the tone of a colour of the easily fusible pigments than is the case in painting upon glass, enamel, fayence, &c. The colours for painting upon porcelain are all of them, *after* the firing, coloured lead glasses throughout; but before this operation, most of them are mere mixtures of a colourless lead glass, the *flux*, and a pigment. In the so-called gold colours, purple, violet and pink, the pigments are preparations of gold, the production of which has hitherto been considered as especially difficult and uncertain. The following are the processes which I employ:—

* Prof. Liebig observes, that the colours for porcelain, described in this paper by Dr. Wæchter, are, judging from samples forwarded to him, of the greatest beauty, and leave nothing to be desired with respect to purity of the tint and comportment in the fire.

Light Purple.

5 grms. of tin turnings are dissolved in boiling nitromuriatic acid, the solution concentrated in the water-bath until it solidifies on cooling. The perchloride of tin prepared in this manner, and which still contains a slight excess of muriatic acid, is dissolved in a little distilled water, and mixed with 2 grms. of a solution of protochloride of tin of 1·700 spec. grav., obtained by boiling tin turnings in excess with muriatic acid to the required degree of concentration. This mixed solution of tin is poured into a glass vessel, and gradually mixed with 10 litres of distilled water. It must still contain just so much acid that no turbidness results from the separation of oxide of tin; this may be ascertained previously by taking a drop of the concentrated solution of tin upon a glass rod, and mixing it in a watch-glass with distilled water.

A clear solution of 0·5 grm. gold in nitromuriatic acid, which must be as neutral as possible, is poured into the solution of tin diluted with 10 litres of water, constantly agitating the whole time. The gold solution should have been previously evaporated nearly to dryness in the water-bath, then diluted with water and filtered in the dark.

On adding the gold solution, the whole liquid acquires a deep red colour, without however any precipitate being formed; this instantly separates upon the addition of 50 grms. of solution of ammonia. But if no precipitate should result, which may happen if the amount of ammonia was too great in proportion to the acid contained in the liquid, and in which case the liquid forms a deep red solution, the precipitate immediately results upon the addition of a few drops of concentrated sulphuric acid. It subsides very quickly. The supernatant liquid should be poured off from it as soon as possible, and replaced five or six times successively by an equal quantity of fresh spring water. When the precipitate has been thus sufficiently washed, it is collected upon a filter; and as soon as the water has drained off completely, removed while still moist with a silver spatula, and mixed intimately upon a ground plate of glass by means of a spatula and grinder with 20 grms. of lead glass, previously ground very fine upon the same plate with water. The lead glass is obtained by fusing together 2 parts of minium with 1 part of quartz sand and 1 part of calcined borax.

The intimate mixture of gold-purple and lead glass is slowly dried upon the same glass plate upon which it had been mixed in a moderately warm room, carefully protected from dust, and when dry rubbed to a fine powder and mixed with 3 grms. of carbonate of silver.

In this manner we obtain about 33 grms. of light purple pigment from 0·5 grm. gold.

The above proportion of lead glass and carbonate of silver to the gold precipitate holds good only for a certain temperature, at which the colour must be burnt-in upon the porcelain, and which is situated very near the fusing-point of silver.

To obtain the colour with a less degree of heat, the amount of lead glass added to the gold must be greater, but that of the carbonate of silver less. The same holds good with respect to the preparation of the purple pigment for glass painting.

The best purple may be spoiled in the baking in the muffle. When this is done at too low a temperature, the colour remains brown and dull; but if the right degree of temperature has been exceeded, it appears pale and bluish. Reducing, and especially acid, vapours, vapours of oxide of bismuth, &c., have likewise an injurious effect upon it.

Dark Purple.

The clear and neutral solution of 0·5 grm. gold in nitromuriatic acid is diluted in a glass vessel with 10 litres of distilled water, and mixed under constant agitation with 7·5 grms. of the solution of protochloride of tin of 1·700 spec. grav., prepared in the manner described above. The liquid is coloured of a dark brownish-red; but the precipitate is only deposited on the addition of a few drops of concentrated sulphuric acid. The supernatant liquid is poured off, and replaced five or six times successively with an equal amount of spring water. The precipitate, which is sufficiently washed, is collected on a filter; and after the excess of water is drained off, removed while still moist with a spatula, and mixed, exactly as described for the light purple, upon a glass plate with 10 grms. of the above lead glass, dried, then reduced to a fine powder, and mixed with 0·5 grm. carbonate of silver; it furnishes about 13 grms. of dark purple pigment. The stated proportion of lead glass and carbonate of silver to the gold is for the same temperature of firing, as given for the mixture of light purple; for a lower temperature, and also for painting upon glass, the quantity of lead glass must be increased and that of the silver salt diminished.

Red-Violet.

The gold precipitate from 0·5 grm. gold is prepared in the same manner as for the dark purple, and whilst moist taken from the filter and mixed intimately upon the plate of glass with 12 grms. of a lead glass, prepared by fusing 4 parts of minium with 2 parts of quartz sand and 1 part of calcined borax; it is then dried as above, and reduced to a fine powder upon a plate of glass, but without any addition of silver. The proportion of lead glass to gold applies likewise for the same degree of temperature as in the case of the light and dark purple pigments; a lower temperature requires a larger proportion of lead glass. A slight addition of silver to this pigment converts the red-violet into a dark purple; and when employed alone for painting upon glass, it gives a very excellent purple.

Blue-Violet.

The same gold precipitate of 0·5 grm. gold is mixed, while still moist, upon the glass plate with 10·5 grms. of a lead glass, obtained by fusing 4 parts of minium with 1 of quartz sand, drying it slowly in the manner above mentioned, and then reducing it to a fine pow-

der upon the glass plate. When the pigment is burnt-in at a lower temperature, a larger addition of lead glass is required. This blue-violet pigment is more especially adapted for mixing with blue pigment. It is not applicable to glass painting. The most important requisite in the preparation of good purple and violet vitrifiable pigment is the very minute state of division of the gold in the gold precipitate, and of the latter in the lead glass, which is accomplished by mixing the moist precipitate with the glass.

By mixing the light purple with the dark purple or with the red-violet, or the red-violet with the dark purple, in different proportions, the artist is able to produce every possible tint of purple and violet. The light purple, without any addition of silver, furnishes an amaranth-red colour, like that seen upon most of the porcelains of the preceding century, when the peculiar property of silver, of converting the amaranth-red into a rose-red colour, does not appear to have been known. Dr. Richter, who at the commencement of this century prepared the pigments for the royal Berlin manufactory of porcelain, appears however to have employed it for his purple, as a very beautiful rose-colour may be seen upon the painted vessels of that time.

Pink.

1 grm. of gold is dissolved in nitromuriatic acid; the solution mixed with one of 50 grms. of alum in 20 litres of spring water; then mixed, constantly agitating, with 1·5 grm. solution of protochloride of tin of 1·700 spec. grav., and so much ammonia added until all the alumina is precipitated. When the precipitate has subsided, the supernatant liquid is poured off, and replaced about ten times successively by an equal amount of fresh spring water; the precipitate is then collected on a filter, and dried at a gentle heat. It weighs about 13·5 grms.; and to prepare the pigment, is mixed with 2·5 grms. carbonate of silver and 70 grms. of the same lead glass described under light purple (2 minium, 1 quartz sand, 1 calcined borax), and reduced to a fine powder on the glass plate.

This colour is only adapted for the production of a light pink ground upon porcelain, and must only be applied in a thin layer; when laid on in a thick layer, the gold separates in a metallic state, and no colour is produced.

All the gold colours above described do not furnish, when fused alone in a crucible, red or violet glasses, as might be expected, but dirty brown or yellowish glasses, which appear troubled from the separation of metallic gold and silver; their peculiar beautiful tint is only developed when they are fused upon the porcelain glaze in a layer which must not be too thick; they then colour it through and through, as a piece of porcelain painted with it shows distinctly in the fracture. If the layer exceeds a certain thickness, the gold and silver separate in a metallic state; and they produce either a liver-colour, as for instance the purple and violet pigments, or no colour at all, as is the case with the more fusible pink pigment.

[To be continued.]

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Metamorphosis of Malic Acid into Succinic Acid. *By* M. Dessaignes.

Asparagine, as shown by M. Piria*, may be regarded as the amide of malic acid. When it is impure and dissolved in water, it soon ferments, and is converted into succinate of ammonia. I conceived that if malic acid or one of its salts was susceptible of experiencing the same kind of fermentation, the relations discovered by M. Piria between asparagine and malic acid would receive a more complete demonstration.

The neutral malate of lime, as obtained by Liebig's process from the berries of the mountain ash, was left under a somewhat deep stratum of water, and in a vessel covered merely with paper, in the autumn of 1847. After three months the water was partly filled with a mucilaginous organized product, in which and upon the sides of the vessel a multitude of beautiful crystals of hydrated carbonate of lime were perceptible. The filtered water furnished a slight precipitate with acetate of lead. The formation of the carbonate of lime and of the mucilage ceased; and as the temperature rose, that is to say, during the spring and summer of 1848, I observed above the malate of lime, which perceptibly decreased, a layer of very delicate aggregated crystals; this layer was heaved up by some large bubbles of gas which had proceeded from the malate of lime. On dissolving these crystals in hot water, precipitating with carbonate of soda and filtration, I obtained a slightly-coloured solution, which precipitated acetate of lead, nitrate of silver, neutral perchloride of iron, and the chloride of barium when mixed with alcohol and ammonia. The concentrated liquid, treated with a slight excess of hydrochloric acid, evaporated to dryness, and the residue frequently exhausted with boiling æther, furnished a solution which left on spontaneous evaporation beautiful colourless prisms of a volatile acid, which burned with flame, leaving no residue upon the blade of platinum; it was, in fact, succinic acid.

The silver salt, well washed and dried at 212°, furnished on calcination 64·80 per cent. of silver; theory requires 65·6. The acid,

* Chem. Gaz., vol. vi. p. 129.

purified by solution in water and dried at 212°, gave on combustion with oxide of copper—

	Found.		Calculated.
Carbon	40·88	..	40·68
Hydrogen	5·25	5·23	5·08
Oxygen	..	..	54·24

The succinic acid represents a considerable part of the weight of the malate of lime submitted to fermentation. I hope soon to determine approximatively the quantity.

Asparagine appears to exist in the young shoots of all the plants belonging to the numerous family of the *Leguminosæ*. All the seeds belonging to plants of this family which I have grown have furnished it in large quantity; I may mention broad beans, French beans, lentils, peas, clover, lucerne, sainfoin, and *Cytisus Laburnum*. What common principle do these seeds contain which is metamorphosed in the act of germination into asparagine? Is it legumine? This question I shall endeavour to solve next spring.—*Comptes Rendus*, Jan. 2, 1849.

Analysis of a native Phosphatic Earth.
By Thornton J. Herapath, Esq.*

This mineral, of which extensive deposits are met with in the greensand and in the lower strata of the chalk formations of Sussex, Surrey, and some few others of our southern counties, was recently sent to my father's laboratory for analysis by a gentleman of Exeter, who desired to know whether it contained any phosphate of lime or other earthy phosphate, as he had been given to understand that it was largely used in commerce by the manufacturers of artificial manures as a substitute for bones, which it equalled, if not excelled, in fertilizing power.

The specimen forwarded to us was a light yellowish-brown, somewhat coarse powder, containing a few larger dark brown siliceous particles. It possessed a specific gravity of 2·981 at 48° F., and was slightly hygrometric.

Qualitative Examination.

When heated to redness on a piece of platina foil, it became darker in colour, and gave distinct indications of the presence of organic matter.

When treated with boiling water, only a very small proportion of it was dissolved, which consisted principally of chloride of sodium and sulphate of soda, with traces of sulphate of lime.

It dissolved with considerable effervescence in boiling dilute hydrochloric acid, giving a bright yellow solution, and left an insoluble siliceous residue, which, even after many hours' digestion, remained of a reddish colour. This, when fused with caustic potash, &c., by

* Communicated by the Author.

Klaproth's process, was found to be almost entirely composed of silica, with a little oxide of iron and alumina.

The acid solution was found to contain phosphoric, sulphuric and silicic acids, with lime, alumina, oxide of iron, and traces of magnesia, oxide of manganese and fluoride of calcium*.

Quantitative Analysis.

A. 150 grs. of the finely-powdered mineral were heated nearly to redness in a platina capsule; the loss amounted to 5·1 grs. in weight = 3·400 per cent.

B. 100 grs. were introduced into Ure's bulb-apparatus, and treated with dilute sulphuric acid; the solution was then heated nearly to boiling, and the whole apparatus placed under the receiver of an air-pump, to expel the remaining traces of carbonic acid; it was then allowed to cool, and weighed. It was found to have lost 12·496 grs. of CO^2.

C.—1. To determine the proportions of the other ingredients, 26·51 grs. of the mineral in fine powder were taken, dissolved in concentrated hydrochloric acid, and the solution evaporated to dryness. The residue was then digested in dilute hydrochloric acid, and the insoluble silica, collected on a filter, washed, dried and ignited, weighed 3·510 grs. = 13·240 per cent.

2. The bright yellow solution was then boiled with a few drops of nitric acid to peroxidize the iron, and afterwards precipitated by a slight excess of chloride of barium. The resulting sulphate of barytes, after being washed, &c., weighed 0·339 gr. = 0·114 gr. SO^3 = 0·430 per cent.

3. The excess of barytes in the filtered solution having been removed by the careful addition of a few drops of dilute sulphuric acid, the solution was filtered, and precipitated by an excess of caustic ammonia; the resulting precipitate was collected on a filter, washed, dried and ignited; it weighed 14·228 grs.

4. It was then redissolved in boiling hydrochloric acid, and reprecipitated by ammonia; the excess of ammonia was then supersaturated by strong acetic acid, the solution boiled, and the insoluble phosphates of iron and alumina washed, dried and ignited, weighed 8·423 grs.

5. These were again redissolved in hydrochloric acid, and the solution boiled with an excess of caustic potash; the insoluble perphosphate of iron having been well washed, &c., was found to weigh 6·564 grs. = 24·760 per cent.

6. The alkaline solution from the preceding was boiled with hy-

* In order to determine the presence of fluorine, a quantity of the mineral in fine powder, weighing about 300 grs., was taken, and introduced into a silver crucible, to which the cover, furnished with a tubulure and bent tube, was afterwards securely luted. About half its weight of strong sulphuric acid was then added, and the mixture moderately heated by means of a spirit-lamp. Upon passing the gas evolved through a small quantity of cold water, a slight but perceptible deposit of silica took place, from the decomposition of the silico-fluoric acid gas, and the solution slightly bleached brazil-wood paper. The proportion of fluorine, however, was too small to be estimated with exactness.

drochlorate of ammonia, and the precipitated phosphate of alumina separated by filtration, washed and ignited, weighed only 0·901 gr. instead of 1·864, as shown by calculation. By treating the solution, however, which had been filtered from the precipitate, with an excess of an acid solution of acetate of iron, a precipitate of perphosphate of iron was obtained, which weighed 1·660 gr. = 0·954 gr. of PO^5. The quantity of phosphate of alumina, therefore, obtained by experiment (0·901 + 0·954 = 1·855 = 6·998 per cent.), differed only by 0·009 from the calculated quantity.

7. The solution containing the earthy phosphates in acetic acid (C. 3.) was precipitated by an excess of peracetate of iron; the insoluble perphosphate of iron, collected on a filter, washed and ignited, weighed 4·659 grs. = 2·677 grs. PO^5* = 10·098 per cent.

8. The iron in the filtered solution having been removed by the addition of ammonia and filtration, the lime was precipitated by oxalic acid; the oxalate of lime, washed, dried and ignited, gave of CaO, CO^2 5·577 grs. = CaO 3·123 = 11·78 per cent.

9. The filtered solution, tested with carbonate of ammonia and phosphate of soda, gave distinct traces of magnesia.

10. The filtrate from C. 2., when precipitated in the usual manner by oxalate of ammonia, &c., gave of CaO, CO^2 7·674 grs. = CaO 4·298 grs. = 16·213 per cent.

11. There were also minute traces of magnesia.

From these results it is evident that the composition per cent. of this mineral is as follows:—

Water	3·400		
Organic matter	traces		
Silica, with some silicate of alumina and silicate of iron	13·240		
Chloride of sodium	traces		
Sulphate of soda	traces		
Carbonate of lime	28·400		
Carbonate of magnesia	traces		
Sulphate of lime	0·736		
Phosphate of lime (tribasic)	21·880	$=PO^5$	10·098
Phosphate of magnesia	traces		
Perphosphate of iron	24·760	$=PO^5$	11·728
Phosphate of manganese	traces		
Phosphate of alumina	6·998	$=PO^5$	4·789
Fluoride of calcium	traces		
Loss	0·586		
	100·000	PO^5	=26·615

* As the results of my experiments on the composition of the perphosphate of iron very closely approximate to those previously published by Drs. Will and Fresenius (Mem. of the Chem. Soc., vol. ii. p. 187), I have assumed the formula of the anhydrous salt to be $2Fe^2O^3 + 3PO^5$. Its composition in 100 parts is therefore—

Sesquioxide of iron	52·632
Phosphoric acid	47·368
	100·000

Judging from the geological position in which these deposits are found, it would appear highly probable that the idea formed by Dr. Buckland with regard to their nature is really correct, namely, that they consist principally of the fossil excretions, or coprolites, of vast numbers of the different carnivorous saurian reptiles, which are known to have inhabited the earth somewhere about this period. This supposition is, moreover, rendered still more probable from the above analysis, showing as it does that the phosphoric acid, an essential constituent in all animal secretions, is present to very nearly as great an extent as in bones*.

According to Mr. Nesbit†, the coprolites from the tertiary deposits of Suffolk contain from 22·30 to 28·74 per cent. of phosphoric acid; another, from the chalk formations, was found to contain 26·92 per cent. These results agree very satisfactorily with the above.

Mansion House, Old Park,
Bristol, January 31st, 1849.

On Hypochlorous Acid and the Chlorides of Sulphur.
By E. Millon.

When chlorine water is preserved in flasks protected from light, it experiences no perceptible change; but if this water is exposed for some time to the influence of the direct rays of the sun, it is found to possess different properties. Thus the chloride of lead is converted by it into brown oxide, and the chloride of manganese gives a black precipitate of peroxide, whilst recently-prepared chlorine water produces no change on these two chlorides. On examining to what chlorinated compound this characteristic oxidation of the chlorides of lead and manganese was to be ascribed, I found that it belonged exclusively to hypochlorous acid; this acid, ClO, may consequently be readily detected even in the midst of a solution of chlorine and in very minute quantity; for these two reagents, especially the manganese test, are extremely delicate.

This action of chlorine upon water is evidently identical with that which it exerts upon most hydrogenous substances; it replaces the hydrogen of the water; and if the phænomenon is limited, it is because the hydrochloric acid in its turn destroys the hypochlorous acid and regenerates chlorine:—

$$2Cl + HO = ClO + HCl \qquad ClO + HCl = 2Cl + HO$$

The hydrochloric and hypochlorous acids can only exist in the presence of a large quantity of water.

The very simple molecular relation which exists between water and hypochlorous acid should, in my opinion, be extended to the chloride of sulphur, which in this system represents sulphuretted hy-

* According to my analysis, the leg-bones of the Ox, after being deprived of their fat and moisture, contain of—

	per cent.	
Phosphate of lime (tribasic)	56·752	= PO^5 27·669
Phosphate of magnesia, with some fluoride of calcium	3·256	

† Quarterly Journal of the Chemical Society, vol. i. p. 233.

drogen in which the hydrogen has been replaced equivalent for equivalent by chlorine. It will be conceived that by this arrangement the highest chloride of sulphur would contain equal equivalents of chlorine and sulphur. The impossibility of combining more than 1 equiv. of chlorine with 1 equiv. of sulphur is well known; whilst, on the contrary, it is easy to unite several equivalents of sulphur with 1 equiv. of chlorine; we have therefore a series corresponding with the polysulphurets of hydrogen, viz.

HO	HS	HS^n
ClO	ClS	ClS^n

Comptes Rendus, Jan. 8, 1849.

Investigation of Ox-bile. *By* A. Strecker.

[Concluded from p. 57.]

Choleic Acid.—Whilst cholic acid is precipitated from the solution of the bile by neutral acetate of lead, a substance containing both sulphur and nitrogen remains in the solution, together with a small quantity of cholic acid, and, after removing the first precipitate, may be thrown down by basic acetate of lead. This sulphurous substance has the properties of a weak acid, and was called by the author in his former paper *choleic acid*. The analyses of the precipitate produced by basic acetate of lead show that it does not always contain the same quantities of oxide of lead, carbon, hydrogen, &c. Even after deducting the oxide of lead, the residual organic substance does not constantly exhibit the same composition,—which was to be expected of a mixture. This precipitate is somewhat soluble in water, especially in boiling water, and dissolves pretty readily in alcohol. But it was found impossible to separate the cholate of lead from the choleate by either of these means. The following plan was therefore adopted to ascertain the composition of choleic acid, by investigating the products of decomposition of the organic substance contained in the lead precipitate, from which, the products of decomposition of cholic acid being known, those derived from choleic acid might easily be determined. The well-washed, dried and pulverized lead precipitate was boiled with barytic water, which removed the greater portion of the lead, and the whole of the organic substance passed into solution. The filtered solution was now mixed with hydrate of baryta, and the hot saturated solution kept boiling for twenty-four hours. The distillate presented the same appearances as with cholic acid; it contained a little ammonia and a substance with a peculiar odour, which rendered the water thickish, and after repeated rectification furnished a few drops of oil.

The residue in the retort was treated in the same manner as in the case of cholic acid. After removing the baryta by a current of carbonic acid, muriatic acid produced a copious resinous precipitate, which in the course of some time became hard and friable. The baryta in the filtered liquid was removed by sulphuric acid, and this and the free muriatic acid by boiling with hydrated oxide of lead,

and the dissolved oxide of lead precipitated by sulphuretted hydrogen. On evaporating the liquid, crystals were left, which possessed the form of taurine, and others that of glycocoll. These two substances were easily and almost completely separated by the employment of alcohol containing muriatic acid, in which the glycocoll is readily soluble, whilst but minute quantities of the taurine are taken up by it. On the spontaneous evaporation of the alcoholic liquid, the muriate of glycocoll is left in long acicular crystals, which are very much like taurine, but differ by the absence of terminal faces.

The insoluble taurine, which was present in larger quantity than the glycocoll, was dissolved in water, and obtained by spontaneous evaporation in large well-formed crystals, which agreed in form and properties with the taurine obtained from ox-bile by means of acids. As however it had hitherto not been known that taurine was formed from a constituent of ox-bile by the action of alkalies, the substance thus obtained was submitted to analysis. The amount of carbon found (19·5 per cent.) and hydrogen (5·8) leave no doubt as to these crystals really being taurine. Besides traces of cholalic acid, taurine and glycocoll, no other substances were contained in the solution.

The precipitate above mentioned, produced by muriatic acid in the barytic solution, proved, from its properties and its analysis and that of its baryta salt, to be cholalic acid, which, on dissolving the washed precipitate in hot alcohol, crystallized in tetrahedrons.

Thus the only products which are formed by decomposing the precipitate produced by basic acetate of lead with baryta are taurine, glycocoll and cholalic acid. Now since the cholic acid contained in this precipitate furnishes, on decomposition with baryta, glycocoll and cholalic acid, the choleic acid simultaneously contained in it must have been decomposed into taurine and cholalic acid. It is evident therefore that choleic acid possesses a similar constitution to cholic acid, only that in the former taurine replaces the glycocoll, which, conjoined with cholalic acid, forms cholic acid. Choleic acid is cholalic acid conjoined with taurine.

Since the formula of taurine and that of cholalic acid are known, the formula of choleic acid may be derived from them; and the different amounts of choleates and cholates which may be obtained from ox-bile furnish a means of testing the accuracy of the formula. For two reasons it appears advisable to ascribe to the choleic acid 2 atoms of water less than the sums of the substances obtained by its decomposition. In favour of this view we have, on the one hand, the analogy with cholic acid, which equally contains 2 atoms less water than the cholalic acid and glycocoll composing it; on the other hand, there is the circumstance that taurine as such does not enter into any combinations with acids, and choleic acid has not in the least the character of a saline compound of cholalic acid with taurine, as the latter can neither be separated from it by alkalies nor acids. Moreover, this view is confirmed by the analysis of mixtures of choleates and cholates. According to these considerations, we have—

Taurine.... $C^4H^7NS^2O^6$
Cholalic acid $C^{48}H^{40}O^{10}$ $\Big\}$ $-2HO$ = choleic acid, $C^{52}H^{45}NO^{14}S^2$.

As just remarked, the analyses of mixtures of choleates and cholates throw further light upon this composition. On comparing the formula of cholic acid, $C^{52}H^{43}NO^{12}$, which contains 2 equivs. of hydrogen less than choleic acid, it is found that if the latter is correctly determined, for 52 atoms of carbon 42 to 44 atoms of hydrogen should have been found in the analysis of the precipitate with basic acetate of lead. Now this is the relation which the author found on analysing the precipitate; and the researches of Theyer and Schlosser and Verdeil contain many such analyses, which according to comparative calculations likewise agree in this respect.

Since, according to Strecker, fresh bile is a mixture of cholates and choleates, these salts prepared directly from the bile, must exhibit the same relation between the carbon and hydrogen. Now it was found that when the bile had not passed into the putrescent state, and the salts had not experienced a partial decomposition by treatment with acids, alkalies or concentrated alkaline earths at a boiling temperature, they all contain for 1 equiv. base 52 equivs. carbon and 42 to 44 equivs. hydrogen. This, for instance, is found in the following baryta salt, obtained by precipitating an aqueous solution of crystallized bile with basic acetate of lead, dissolving the washed precipitate in alcohol, decomposing it with sulphuretted hydrogen, and after expelling the sulphuretted hydrogen, mixing it with a slight excess of barytic water. Carbonic acid was passed into the solution, which was then evaporated to dryness; the residue was treated with alcohol, and this removed by evaporation. The baryta salt prepared in this manner—a mixture of cholate and choleate of baryta—was dried at 248° and submitted to analysis, when it was found to contain in 100 parts,—carbon, 55·4; hydrogen, 7·73; baryta, 13·69; according to these numbers, for every equivalent of baryta there is 51·5 equivs. carbon and 43·2 equivs. hydrogen.

Similar baryta salts have been analysed by Mulder, but not recognised to be mixtures, and described as bilifellinate of baryta; his analytical results agree with the above relation, as the numerical results contained in the original equally prove.

Lastly, the same relation between carbon and hydrogen must be again met with, supposing the above view of the constitution of the bile to be correct, when the purified bile, that is to say the precipitate produced by æther in an alcoholic solution of bile, is analysed. Sometimes the whole mass of this precipitate crystallizes. That which falls first contains most choleates. In general, in such analyses the ashes must not be taken into consideration, because they contain not only soda, but variable quantities of potash, ammonia, magnesia, &c. The soda may to a certain extent have been originally present in the bile as carbonate, since the ash has an alkaline reaction; but the disengagement of carbonic acid, which takes place on treatment with acids, is principally due to the decomposition of the cyanates, which are contained in the ash along with sulphate of soda.

The analysis of a crystallized bile, which was once obtained without any perceptible amount of potash and ammonia, gave the following numbers. In calculating the atomic relations, the amount of sulphur, 2·7 per cent., has been taken as basis; according to which for 0·43 choleate of soda there is 0·57 equiv. cholate of soda. The results were—

	Found.	Atomic relations.	Calculated.
Carbon.....	60·55	51·50	61·3
Hydrogen	8·63	44·00	8·4
Nitrogen	2·52	0·92	2·7
Oxygen			
Sulphur	2·70	0·43	2·7
Soda.....	6·08	1·00	6·0

On account of the variation in the constituents of the ash, the author has likewise analysed a bile, in which he endeavoured to replace as it were the mixture of bases by a single base, potash. A solution of caustic potash was added to an aqueous solution of bile, the precipitated potash salt collected on a filter, washed with solution of potash, and dissolved in absolute alcohol. Dry carbonic acid was passed into the solution for a considerable time, the precipitate collected on a filter, and æther added to the solution. The precipitate which first formed had an alkaline reaction, owing to some adherent carbonate of potash which had remained dissolved in the alcohol; the liquid was therefore separated from it, and now completely precipitated with æther. After standing for some time, the precipitate was converted into acicular crystals; they were dried at 212°, and submitted to analysis, when they gave—

	In 100 parts.	Atomic relations.
Carbon.....	59·02	51·6
Hydrogen.....	8·33	43·6
Potash	8·97	1·0

Lastly, the analyses of a soda salt, prepared by decomposing the precipitate by basic acetate of lead with carbonate of soda, solution in absolute alcohol and precipitation with æther, agree with the above-calculated relation of 52 equivs. C to 42 to 44 equivs. H. The substance, dried at 212°, gave—

			Atomic relations.	
	I.	II.	I.	II.
Carbon.....	62·18	62·59	51·9	51·4
Hydrogen.....	8·72	8·82	43·6	43·5
Soda	6·19	6·28	1·0	1·0

Although the author's view regarding the constitution of bile may be looked upon as proved, still the properties of one of the principal constituents of the bile, viz. the choleate of soda, are but very imperfectly known. Nevertheless, the author, by examining the bile of other animals, especially the bile of fishes, which consists almost entirely of cholcates with very little cholates, and by studying the substance obtained by repeatedly precipitating ox-bile with æther,

and only collecting the first portion, in which the amount of choleates is increased, made the following observations on these salts. They show that *choleic acid*, on treatment with alkalies, is decomposed into cholalic acid and taurine; and consequently that the bile, on similar treatment, must separate into cholalic acid, taurine and glycocoll; and that the bile, on treatment with acids, is likewise decomposed into taurine and glycocoll (which remain dissolved in water), and according to the duration of the action, into choloidic acid and dyslysine (both insoluble in water).

Properties of the Choleates.—The salts with alkaline bases are readily soluble in alcohol and water and insoluble in æther; they have no action upon litmus-paper, increase considerably in weight in moist air, but do not deliquesce. When left for a long time in contact with æther, they are throughout the entire mass changed into radiating groups of crystals. When heated upon platinum foil, the salt melts, puffs up and burns with a luminous smoky flame, leaving a very fusible ash. The aqueous solution has a very sweet taste, with a bitter after-taste. No precipitate is produced in it by acids, even by concentrated sulphuric acid; the solution, mixed with acid, may be heated to boiling for a moment without becoming turbid, but after a short time oily drops of choloidic acid separate, which subsequently harden; the solution then contains taurine. Upon the addition of concentrated caustic potash to the aqueous solution of the choleate of potash, the whole of the potash salt separates. The potash salt is also separated by a carbonated alkali, but not by a sulphate or muriate. Carbonic acid separates no alkali from an alcoholic solution of an alkaline choleate. No precipitate is produced with salts of lime, baryta or magnesia, not even upon the addition of ammonia. Neutral acetate of lead produces no turbidness, but the basic acetate separates white flakes, which soon unite to a plaster-like mass. This precipitate dissolves completely on boiling, and again separates on cooling. A large excess of basic acetate of lead also dissolves it entirely. After the precipitate with basic acetate of lead has subsided, ammonia causes another precipitate similar to the first; but a considerable quantity of choleic acid remains in solution. On removing the lead with sulphuretted hydrogen and concentrating, a further precipitate may be obtained with basic acetate of lead. Both the aqueous and alcoholic solutions of choleates may be evaporated in the water-bath without their properties being altered, nor do they experience any change upon long exposure to the air if they are pure; but a solution of the free acid, as obtained by decomposing the lead salt with sulphuretted hydrogen, cannot be evaporated to dryness without decomposition; the residue no longer gives a clear solution with water, and when dissolved in alkalies furnishes a precipitate with dilute acids. It appears probable that, in this decomposition of the choleic acid, before the separation into taurine and non-nitrogenous acids has taken place, intermediate products are formed, which differ from choleic acid by a less amount of water. These products are soluble in pure water, but are precipitated from the solution by acids.

Acetate of copper produces no precipitate in aqueous solutions of the alkaline choleates; a little ammonia separates bluish-white flakes, which are dissolved by more ammonia. Nitrate of silver gives no precipitate, not even on the addition of ammonia; on boiling, a portion of the silver is reduced. Perchloride of iron produces at first a precipitate, which on the addition of more perchloride disappears. Perchloride of mercury gives no precipitate; protonitrate of mercury and protochloride of tin separate white flakes. When heated with sulphuric acid and sugar, these salts exhibit the same violet-red colour as the cholates.

The products of decomposition which bile furnishes when it is allowed to putrefy and is not freed from mucus, are very similar to those obtained by means of alkalies and acids. In the hot months of summer a putrid odour appears in less than twenty-four hours. Acetic acid now produces a precipitate in a solution of the bile. Any putrescent animal or even vegetable substance, for instance synaptase, produces the same effect as the mucus of the gall-bladder. In an aqueous solution of purified bile no such decomposition takes place.

The biline of Berzelius has many properties in common with the alkaline choleates, cholanic acid with a mixture of choloidic acid and a little cholic acid, and the cholic acid of Berzelius with cholalic acid.

Since, from all the facts hitherto enumerated, it is evident that the two acids of the bile have originated by the conjunction of a single acid, cholalic acid, in one case with glycocoll, in the other with taurine, it is important to assign a place in the system to this acid; but there are few acids with which it appears to stand in any close relation; these are lithofellinic acid, lichesteric acid and rocellic acid.—*Ann. der Chem. und Pharm.*, lxvi. p. 1.

On some Binary Compounds formed by the Metalloids, and in particular on the Action of the Perchloride of Phosphorus upon Sulphurous, Sulphuric, Phosphoric and Chromic Acids, &c. By M. Persoz.

Phosphorus being a substance eminently susceptible of oxidation, it appeared *à priori* that on bringing the perchloride of phosphorus or the protochloride into contact with concentrated nitric acid or with nitrates, the radical would be oxidized at the expense of the oxygen of the nitric acid, and that the nascent chlorine in the presence of nitrogen, likewise in a nascent state, would be in the most favourable condition for uniting with the latter body and producing the perchloride of nitrogen; but on making the experiment with concentrated nitric acid and the perchloride of phosphorus in a tube, sealed before the lamp, I soon found that the reaction was by no means so simple as I had supposed.

The oxidation of the phosphorus and the formation of phosphoric acid are incontestable; but the chlorinated compound, instead of consisting simply of chlorine and nitrogen, always contains a certain

amount of oxygen, and is related to, if not identical with, the products from *aqua regia* recently investigated by M. Gay-Lussac, when the reaction is effected under certain circumstances.

Nitrous acid, in contact with the perchloride of phosphorus, furnishes anhydrous phosphoric acid and a complex chloroxynitrous compound. Nitric and nitrous acids, when brought into contact with the protochloride of phosphorus, produce a very lively reaction, which is always accompanied by a loud explosion.

With the view to ascertain whether the perchloride of phosphorus was capable of reducing certain oxidized compounds, I acted with it upon sulphuric, sulphurous and phosphoric acids; but instead of having a double displacement of the compound elements, I obtained a simple combination of the binary compounds; thus, according as the perchloride of phosphorus is made to act indirectly upon the sulphuric acid by passing this chloride into persulphate of mercury suitably heated in a glass tube, or the chloride is passed directly into anhydrous sulphuric acid, there is obtained in the first case a compound represented by $Cl^{10} P^2 + SO^3$, and in the second case a compound represented by $Cl^{10} P^2 + 2SO^2$.

These compounds are liquid at the ordinary temperature, and are volatilized at fixed temperatures; water decomposes them into sulphuric, phosphoric and hydrochloric acids.

On passing pure dry sulphurous gas into the lower portion of a retort containing perchloride of phosphorus, and furnished with a receiver, these two substances soon disappear, giving rise to a white liquid, which is volatilized without decomposition, and which, when suitably purified, may be represented by $Cl^{10} P^2 + SO^2$. This compound, in contact with water, at first furnishes substances which would be produced directly by the action of this agent upon the perchloride of phosphorus, *i. e.* hydrochloric and phosphoric acids, then sulphurous acid; for on decomposing the new substance with water, a liquid is obtained which possesses all the properties of a solution of sulphurous acid; in fact, it reduces the manganates, the chromates, the iodates, and lastly, it does not precipitate an acid solution of chloride of barium; on the other hand, it furnishes an abundant precipitate when previously treated with chlorine.

When the vapour of perchloride of phosphorus is passed over a stratum of anhydrous phosphoric acid, combination takes place, a colourless liquid compound is formed, which possesses a fixed boiling-point, and is decomposed by water into hydrochloric and phosphoric acids. The analysis which I have made of a portion of this compound still containing a small quantity of perchloride of phosphorus, leads me to think that it should be represented by $Cl^{10} P^2 + P^2 O^5$. I have also obtained several compounds of the same kind, by substituting other chlorides for the perchloride of phosphorus, and the above anhydrous oxyacids by other oxygenous and non-oxygenous compounds acting the same part, and likewise anhydrous. Everything leads me to think that we shall succeed in discovering a number of combinations of the second order formed by binary compounds. The crystalline compound obtained by M. Kuhlmann, by

acting with nitric oxide upon the perchloride of tin, is probably only one example of the compounds we have indicated.—*Comptes Rendus*, Jan. 15, 1849.

On the Solid and Volatile Fatty Acids of Cocoa-Nut Oil. *By* A. Georgey.

The existence of caproic acid, $C^{12} H^{12} O^4$, and of capryllic acid, $C^{16} H^{16} O^4$, in cocoa-nut oil was demonstrated by M. Fehling. The author's object was to ascertain the presence of capric acid, $C^{20} H^{20} O^4$, in this substance; for which purpose it was saponified with a dilute solution of potash and the soap decomposed with weak sulphuric acid. On submitting the acid liquid to distillation, it first furnished a milky product; after which the liquid collected in the receiver became clear, and separated entirely from the fat which passed over at the same time; when this change occurred the distillation was stopped, and the distilled acid liquid neutralized with potash. The soap thus obtained was purified by precipitation with chloride of sodium, then redissolved in water, and decomposed with weak sulphuric acid. In this way a mixture of fatty acids, both liquid and solid, at the ordinary temperature, was obtained floating upon the mother-liquors in the form of a layer of fat.

In this mixture of acids the author sought for the pichuric, capric and caproic acids. He adopted the following plan for isolating them:—The ammoniacal solution was decomposed with chloride of barium, the precipitate suspended in a large quantity of water and boiled. If the filtered liquid becomes turbid while still warm, and deposits light, bulky, white flakes, we may be assured of the presence of pichuric acid. If, on the contrary, the precipitate only separates upon cooling in the form of a fine white powder, there is positive proof of the presence of capric acid. The pichurate of baryta is less soluble than the caprate, and is deposited before it; whence the possibility of separating these two salts, especially on operating upon large quantities. The author first submitted these salts to repeated crystallization from water, and then from alcohol; and did not consider them pure until perfectly accordant results were obtained in estimating the amount of baryta in the same salt, crystallized first from water and then from alcohol.

The author was able to isolate in this manner the caprate of baryta, $C^{20} H^{19} O^3$, the composition of which he confirmed. The capric acid, separated from this salt by means of tartaric acid, is solid at the ordinary temperature and somewhat fatty to the touch. It melts at 86°; in the solid state it has a very faint smell of goat, which becomes stronger when it is melted. It is perceptibly soluble in boiling water, and separates as the solution cools in minute crystalline laminæ. With oxide of silver it forms a salt, the composition of which is expressed by the formula $C^{20} H^{19} O^3 + AgO$.

Capric acid exists but in small quantity in cocoa-nut oil; according to the author, the chief principle of this vegetable fat is pichuric acid; the baryta salt of which being less soluble than the

caprate, is precipitated in the form of snowy-white bulky flakes. Pichuric acid is solid. When a concentrated alcoholic solution of this acid is cooled to 32°, it is obtained in warty masses consisting of agglomerations of slender needles. The specific gravity of solid pichuric acid is 0·883 at 68°. Its melting-point is situated between 108° and 110°. Its composition is expressed by the formula $C^{24} H^{24} O^4$; it was checked by the analysis of the baryta salt, $C^{24} H^{23} O^3$, BaO, and by that of pichuric æther, $C^{24} H^{23} O^3$, $C^4 H^5 O$.

In the retort in which the soap from the butter of cocoa had been distilled with sulphuric acid, a fixed residue is left, consisting of a mixture of fatty acids with high equivalents. The author made some experiments to determine their nature; and he is led to admit the presence of myristic and palmitic acids. The butter of cocoa would consequently contain the following acids:—

Caproic acid	$C^{12} H^{12} O^4$
Capryllic acid.....	$C^{16} H^{16} O^4$
Capric acid.....	$C^{20} H^{20} O^4$
Pichuric (lauric, laurostearic) acid	$C^{24} H^{24} O^4$
And probably myristic acid	$C^{28} H^{28} O^4$
And palmitic acid	$C^{32} H^{32} O^4$

In conclusion, the author observes that these results are directly opposed to those obtained by St. Evre* in his investigation of cocinic acid. According to M. Georgey, the cocinic acid of M. St. Evre, $C^{22} H^{22} O^4$, is a mixture of capric acid, $C^{20} H^{20} O^4$, and of pichuric acid, $C^{24} H^{24} O^4$; its melting-point, situated at 95°, is nearly the mean between the melting-points of capric, 86°, and pichuric, 108°. After having tried all the processes of purification applied to mixtures of the fatty acids of the cocoa-nut oil, the author arrives at the conviction that the only one which admits of pure products being obtained consists in crystallizing the salts of baryta.—*Ann. der Chem. und Pharm.*, lxvi. p. 298.

ANALYTICAL CHEMISTRY.

On some new Applications of Sulphuretted Hydrogen in Chemical Analysis. By M. Ebelmen.

Hitherto sulphuretted hydrogen has rarely been employed in analysis, except to precipitate certain metals from their solution in acids. In many cases this substance is one of the most accurate and handy reagents known. The facts contained in the present paper will show that it may likewise be used with considerable advantage for separating certain substances one from the other by converting them in the dry way into sulphurets. It may then happen that one of the sulphurets formed is not acted upon by acids, while the other is; it may also happen that one of the sulphurets is volatile, and is separated from the other by the employment of a somewhat elevated temperature. I have employed this method in solving several

* See Chem. Gaz., vol. v. p. 328.

problems of chemical analysis, the solution of which by our present means was not quite satisfactory. I shall now proceed to give the results obtained.

1. *Separation of Manganese from Cobalt.*—A considerable number of methods have been proposed for the separation of these two metals. The most accurate, according to Rose, would consst converting the two oxides into protochlorides, by heating them in a current of hydrochloric acid gas, and treating the protochlorides at an elevated temperature with hydrogen. The protochloride of cobalt is alone reduced to the metallic state, so that water merely dissolves the protochloride of manganese. This method is complicated and not quite accurate; a little oxide of manganese always remains with the cobalt. It has recently been proposed to treat the solution of the two oxides in hydrochloric acid with an excess of carbonate of baryta, and then to pass into the neutralized liquid a current of sulphuretted hydrogen, which was said to precipitate only the cobalt in the state of sulphuret. I found that the cobalt was precipitated, it is true, before the manganese, but that the latter metal was entirely thrown down in the presence of carbonate of baryta by the sulphuretted hydrogen; it is consequently impossible to separate these two metals by this process.

The method which I have employed to solve the question is simple and very expeditious; it is founded on the fact, that the sulphuret of cobalt prepared in the dry way is not in the least acted upon by cold dilute hydrochloric acid, which does not apply to the sulphuret of manganese. I proceed as follows:—After having weighed the mixture of the two oxides to be separated, it is placed in a platinum or porcelain tray, and heated in a current of sulphuretted hydrogen. The action begins at the ordinary temperature. The mixture of the two oxides gives off considerable heat in the gas. The tube containing the two oxides is then raised to a dark red heat; the sulphuret is allowed to cool in a current of the gas, the tray drawn out of the tube, and digested in cold water containing a little hydrochloric acid. The sulphuret of manganese alone is dissolved. After some hours' digestion it is filtered, the liquid boiled, precipitated with potash, and the oxide of manganese determined. The black residue of sulphuret of cobalt is redissolved in nitric acid, and this solution also precipitated by potash. The following experiments will serve to show the accuracy of the process:—

First Experiment.—A mixture of

Red oxide of manganese	0·300 grm.
Protoxide of cobalt.....	0·300 ...

was dissolved in hydrochloric acid, the whole precipitated with potash, and the precipitate washed carefully and calcined; it weighed with the ash of the filter 0·611. It was then heated on a porcelain tray in sulphuretted hydrogen, the sulphurets digested for twelve hours in cold very dilute hydrochloric acid, and then filtered; the filtered liquid was perfectly colourless, and on treatment with potash gave 0·302 red oxide of manganese. The residue of sulphuret of cobalt

was decomposed with nitric acid, and the filtered solution precipitated with potash; it gave 0·303 protoxide of cobalt. The red oxide of manganese, on examination before the blowpipe, gave with borax a perfectly colourless bead in the reducing flame, which proved that it contained no cobalt. The oxide of cobalt, treated with nitre and potash in a silver crucible, did not exhibit the least sign of the presence of manganese.

Second Experiment.—A mixture of

Red oxide of manganese	0·481 grm.
Protoxide of cobalt	0·090 ...

treated as in the preceding experiment, gave

Red oxide of manganese	0·486 ..
Protoxide of cobalt	0·092 ...

Both the oxides were ascertained to be free from each other.

Third Experiment.—A mixture of 0·023 grm. red oxide of manganese and 0·980 protoxide of cobalt gave, on similar treatment, 0·028 oxide of manganese; the cobalt was not estimated. The oxide of manganese gave a perfectly colourless bead with borax in the reducing-flame of the blowpipe. Dissolved in a small quantity of hydrochloric acid, it furnished a perfectly colourless liquid, which gave with hydrosulphate of ammonia an orange-coloured precipitate. The least trace of cobalt would have blackened it.

The slight excess found in the estimation of the manganese, and which is apparent in all the experiments, appears to be attributable to a small quantity of foreign substances in the alkaline solution used to precipitate the cobalt and manganese. The difficulty of obtaining alkalies absolutely free from silica or alumina is well known. It was also found that the cobalt and manganese from the preceding experiments always left a slight insoluble residue when treated with hydrochloric acid after having been calcined and weighed.

Fourth Experiment.—A mixture of 0·963 grm. red oxide of manganese and 0·012 protoxide of cobalt afforded on similar treatment 0·012 oxide of cobalt; the manganese was not determined. The oxide of cobalt did not contain a trace of manganese.

The two last experiments show that the process may be employed for the accurate separation of cobalt and manganese, even in the case where one of the metals greatly preponderates over the other. It may be applied directly in examining ores of manganese for oxide of cobalt. It would suffice to heat them in a current of sulphuretted hydrogen, and then act upon them with very dilute hydrochloric acid. The whole of the cobalt will be contained in the insoluble residue.

Separation of Manganese and Nickel.—This is effected by the same method as that for manganese and cobalt. A mixture of

Protoxide of nickel	0·179 grm.
Red oxide of manganese	0·321 ...

was dissolved in hydrochloric acid, precipitated with potash, the

precipitate calcined, heated in sulphuretted hydrogen, and treated with cold very dilute hydrochloric acid. There was found—

Oxide of nickel	0·178 grm.
Red oxide of manganese	0·320 ...

The results are consequently as precise in this case as in the separation of cobalt from manganese.

Separation of Manganese and Zinc.—I have attempted to apply the above process to the separation of zinc and manganese. As the sulphuret of zinc dissolves with time in dilute hydrochloric acid, I treated the mixture of the two sulphurets prepared in the dry way with acetic acid, the action of which was assisted by heat. In this way only the manganese is dissolved, but the sulphuret of zinc retains a small quantity of manganese which cannot be separated by this method. When operating with weighed quantities of zinc and manganese, I have always obtained too large an amount of oxide of zinc, and have found it to contain a certain quantity of oxide of manganese.

Separation of Iron and Cobalt.—When a mixture of peroxide of iron and cobalt is heated in sulphuretted hydrogen, and then acted upon even with concentrated hydrochloric acid, scarcely any iron is removed; the sulphuret of cobalt retains nearly the whole of the sulphuret of iron.

As the sulphuret of iron, which is obtained by heating peroxide of iron to a nascent red in sulphuretted hydrogen, is not acted upon by dilute cold hydrochloric acid, I imagined that this property might be turned to account for separating iron from manganese; but experiment has shown that the sulphuret of iron always contains a considerable proportion of sulphuret of manganese.

The volatility of certain sulphurets furnishes a means of separation which may be turned to account in some cases. I will mention two examples, the one relative to the separation of iron and arsenic, the other to the separation of arsenic and tin.

Separation of Iron and Arsenic.—When arseniate of iron is heated in a current of sulphuretted hydrogen, both the iron and arsenic are completely sulphurized; but the latter body is entirely volatilized. The separation is very accurate. A mixture was made of

Metallic iron....	1·330 grm., corresponding to peroxide,	1·900
Arsenious acid ..	1·380 grm., corresponding to arsenic acid,	1·711
		3·611

The two bodies were dissolved in *aqua regia*, the solution precipitated with ammonia in excess; the precipitate, dried and carefully removed from the filter, weighed after calcination 3·315; the filter and adherent matter were calcined separately in a porcelain crucible, and gave 0·055 = 3·370, which number is considerably lower than that which ought to have been obtained if the whole of the arsenic had been precipitated with the peroxide of iron. I found that a very considerable quantity of arsenic remained in the ammoniacal solution, but not a trace of iron. It amounted to 0·241 grm.

or 14 per cent. of the total quantity. 3·370 arseniate of iron must therefore contain—

Peroxide of iron.....	1·900 grm.	56·4 in 100 parts
Arsenic acid	1·470 ...	43·6 ...
	3·370	100·0

which composition corresponds very nearly to the formula AsO^5, $2Fe^2O^3$.

0·788 grm. of this arseniate was heated to a faint red heat in sulphuretted hydrogen. A large quantity of sulphuret of arsenic was volatilized. The sulphuret of iron which remained was of a greenish-yellow colour, and possessed a certain metallic lustre; it weighed 0·6065. On dissolving it in nitromuriatic acid, precipitating with ammonia, it gave 0·444 peroxide of iron, which proves that the arseniate contained—

Peroxide of iron	0·444 grm.	56·3 per cent.
Arsenic acid (from the loss)	0·344 ...	43·7 ...
	0·788	

The peroxide of iron was dissolved in hydrochloric acid; the solution, boiled with sulphurous acid and treated with sulphuretted hydrogen, gave not a trace of sulphuret of arsenic.

Second Experiment.—1·050 grm. of the same arseniate of iron, treated as above, gave—

Peroxide of iron	0·594 grm.	56·5 per cent.
Arsenic acid.....	0·456 ...	43·5 ...
	1·050	

The peroxide of iron, examined as in the preceding experiment, did not give a trace of arsenic.

It is seen that the results of these two experiments agree very well with each other, and with those deduced synthetically; they perfectly establish the accuracy of the method. The native arseniates of iron may be directly analysed by this method. It may also probably be applied without modification to the direct analysis of the arseniates of cobalt, nickel, zinc, copper and lead.

When a current of sulphuretted hydrogen is passed over heated perphosphate of iron, it is merely changed into the protophosphate, which dissolves without residue in hydrochloric acid, and without exhibiting any disengagement of sulphuretted hydrogen.

Separation of Arsenic and Tin.—The separation of arsenic and tin is considered to be one of the most difficult problems of analytical chemistry. Professor Rose states, in his work on Analytical Chemistry, that he is not acquainted with any good method of separating these two substances. The plan recently proposed by M. Levol* is very complicated. I have applied the method above given for the separation of iron from arsenic to the separation of arsenic from tin; and the following experiments will show that the pro-

* Chem. Gaz., vol. iv. p. 159.

cess is susceptible of very great accuracy. I weighed off 0·495 grm. of fine tin, corresponding to 0·629 stannic acid, and 0·233 arsenious acid. The two substances were treated with hot nitric acid, evaporated nearly to dryness, then mixed with water. The oxide of tin weighed after calcination 0·746; it consequently contained 0·117, or 15·7 per cent. of its weight of arsenic acid; the rest of the arsenic had remained in solution. Of this 0·746 grm. arseniate of the oxide of tin I took 0·347, and heated it upon a porcelain tray in a current of sulphuretted hydrogen. A considerable quantity of sulphuret of arsenic sublimed; the residue appeared to be a mixture of bisulphuret of tin and of a lower sulphuret. Roasted and then strongly calcined in a platinum crucible, this residue of sulphuret left 0·286 stannic acid, or 82·4 per cent. According to synthesis 84·3 should have been found; but this slight difference is readily explained from the difficulty of obtaining absolutely pure tin. I assured myself, by reducing the 0·286 stannic acid and treating the tin obtained with hydrochloric acid, that the sulphuret of tin had not retained a trace of arsenic. The arsenic was not determined, but it would have been easy to have done so, as the whole of the sulphuret of arsenic was contained either in the tube or in the water into which the tube dipped. This method therefore appears applicable to the analysis of the arseniates of tin, and it may probably also be applied to the direct analysis of the arseniuret of tin. This substance, when exposed to the action of sulphuretted hydrogen, parts with the arsenic in the state of sulphuret; and the sulphuret of tin which remains is readily converted into stannic acid by roasting.—*Ann. de Chim. et de Phys.*, Jan. 1849, p. 92.

On a new Test for the Proteine Compounds. *By* E. Millon.

The very acid liquid which is obtained by dissolving mercury in its weight of nitric acid with $4\frac{1}{2}$ equivs. water is an extremely delicate reagent for all albuminous substances, and for a large number of the secondary products related to them. This liquid communicates to these substances a very deep red colour; and in this manner a one-hundred-thousandth part of albumen in water, and even less, may readily be detected.

To give an idea of the delicacy of this test, and also of its probable use in the study of vegetable productions, I may state that cotton, starch and gum-arabic acquire a very distinct rose-colour in contact with it. Urines are nearly all of them coloured red after the nitro-mercurial liquid has been mixed with them, and the mixture heated to destroy the gelatine. The albumen of the blood and of vegetables, fibrine, caseine, gluten, legumine, silk, wool, feathers, horn, epidermis, gelatine, chondrine, proteine, crystalline, the well-washed buffy coat of the blood, both the soluble product which it parts with to boiling water, as well as the insoluble portion, are all of them coloured more or less deep red.

When proteine is rendered soluble by the prolonged action of alkaline solutions or by the action of sulphuric acid, the same red

colour is constantly produced; but it is no longer an insoluble substance which is obtained; the liquid becomes deep red, without giving any precipitate.

Xanthoproteic acid, the chlorites, and the oxides of proteine which are derived from the chlorites, differ from the preceding products; they are not in the least coloured red; consequently the buffy coat of the blood is not identical with the oxides of proteine obtained by acting with potash on chlorites of proteine. This reagent therefore enables us to investigate some very interesting differences. I have already ascertained that the action of chlorine upon albumen until the gas ceases to be absorbed furnishes no less than three very distinct substances.

The nitromercurial solution is prepared by pouring an equal weight of nitric acid with $4\frac{1}{2}$ equivs. water upon the pure metal; a lively reaction instantly ensues. When it slackens, a gentle heat is applied until the whole of the metal is dissolved; 2 vols. of water are then added for 1 of the mercurial solution. After some hours, the liquid above the crystalline mixture of protonitrate and protonitrite of mercury is decanted. This liquid reacts in the cold upon the albuminous substances, but the reaction is only perfect between 140° and 160°; it is even advisable to boil the mixture at once. Long-continued contact with an excess of the reagent does not affect the red substance. I have preserved for more than a year some albumen of an intensely red colour in a large excess of the nitromercurial liquid.

It should be observed, that the peculiar property of the reagent does not reside either in the protonitrate or in the pernitrate of mercury, nor in a mixture of the two; it is necessary that the solution containing these two salts should also contain nitrous acid; otherwise no colouring is produced. The pure pernitrate of mercury, saturated with nitrous acid, has a perceptible reaction; but it is not to be compared to that of the mixture of the two salts saturated with nitrous acid; consequently the best method of preparing this reagent is according to the directions above given.—*Comptes Rendus*, Jan. 8, 1849.

Method of detecting the Flour of Indian Corn in that of Wheat. *By* M. Mauviel la Grange.

The sample is sifted, and 2 grms. of the finest flour mixed in a test-tube with 4 grms. of nitric acid, and well stirred with a glass rod. After this add 60 grms. of water, and then 2 grms. of carbonate of potash dissolved in 8 grms. water. When no Indian corn is present, as soon as the carbonic acid has escaped only yellowish flakes separate; but when any Indian corn is present, some orange-yellow particles subside, which are easily detected. In this way an admixture of from 4 to 5 per cent. of Indian corn with wheaten flour may be detected.—*Journ. de Chem. Méd.*, iv. p. 339.

THE CHEMICAL GAZETTE.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

Observations on the Lactic Acid of Flesh. *By* Dr. W. Heintz.

Liebig prepared from the fluids of the flesh of animals an acid which has exactly the per-centage composition of lactic acid, and does not appear to differ from it in its properties. But he found that the salts of the two acids differed in the amount of water they contained; for instance, the zinc salt from the acid prepared from flesh contains only 2, and the lime salt 4 atoms of water; whilst the corresponding salts of the acid prepared from milk combine with 3 and 5 atoms of water of crystallization. Liebig was of opinion that the differences in the amount of water in these salts were probably owing merely to the different mode of preparation, and that the acid obtained from flesh was nevertheless lactic acid. He was the more justified in doing this, as both the composition, as well as the known properties, of the two acids, and even of their salts, coincided completely; and the differences in question were of such a nature that they might be explained in a more simple manner than by assuming an isomeric modification of lactic acid with almost identical properties.

Recently Engelhardt* however has proved that these differences in the amount of water which the salts of the two acids contain are really constant; that their salts are essentially distinguished by different degrees of solubility in water and alcohol, and that they cannot therefore be regarded as identical. He is of opinion that the cause of the different properties of these acids may be owing to the circumstance that the one obtained from flesh is a monobasic acid, whilst the bibasic nature of the lactic acid prepared from sugar had been incontrovertibly proved by Maddrell and himself in a former investigation. Want of material however prevented him from ascertaining the truth of this supposition.

On perusal of his paper, the view which he proposes did not appear to me the only one conceivable. I considered it possible that the acid from muscular flesh might contain less oxygen and hydrogen in the proportion to form water than lactic acid from milk; but that from the salts hitherto examined, only so much water could be expelled at the temperature employed for their desiccation, that, in

* Chem. Gaz., vol. vi. p. 298.

the salt, for 6 atoms of carbon 5 atoms of hydrogen remained instead of 4 or 3. To affirm or refute this view, I have made the following experiments; but unfortunately the quantity of material at my disposal was too small for me to extend them further. In the first place, I had to assure myself that the acid employed in my experiments, and which had been prepared from horse-flesh, was distinguished from lactic acid by the above differences. I therefore selected the zinc salt for my experiments, which had been prepared by saturating the acid with carbonate of zinc and slow evaporation. At 212° it very slowly parted with 13·04 per cent. of water of crystallization; this was effected more rapidly between 212° and 248°; 2 atoms would require a loss of 12·90. The dried salt afforded on combustion—

Carbon	29·44	6	29·63
Hydrogen	4·24	5	4·11
Oxygen	32·92	5	32·93
Oxide of zinc	33·41	1	33·33

The composition of the salt therefore is expressed by the formula $C^6 H^5 C^5, ZnO + 2HO$.

Lactate of zinc prepared from milk, and which had also separated by gradual evaporation, lost, on the contrary, between 230° and 248°, 18·22 per cent. water; theory requires 18·18 for 3 atoms. The dry salt afforded on combustion—

Carbon	29·61	6	29·63
Hydrogen	4·19	5	4·11
Oxygen	32·86	5	32·93
Oxide of zinc	33·34	1	33·33

numbers which lead to the formula $C^6 H^5 O^5, ZnO + 3HO$.

These experiments not only prove the identity of the acid with that employed by Liebig and Engelhardt, but they also confirm its distinctness from lactic acid. In order to ascertain whether from other salts of these acids, besides the zinc and lime salts, which alone had been more minutely studied, so much water might be expelled that after drying, less than 5 atoms of hydrogen would remain for 6 atoms of carbon, I have prepared and analysed those compounds which are usually obtained anhydrous, the lead and the silver salts.

The first was obtained by boiling the free acid with an excess of hydrated oxide of lead, filtering the liquid from the insoluble portion, and evaporating it slowly. In this operation it became slightly turbid, on which account it was again evaporated to dryness, and the residue dissolved in water; an insoluble grayish powder remained, which however contained neither carbonic acid nor organic substance in considerable quantity, and consisted therefore essentially of oxide of lead. The solution, again evaporated to dryness, exhibited not a trace of crystallization, but formed a transparent gummy mass, which, kept for some length of time at 248°, became hard and fissured after cooling, whilst upon being again heated it fused to a liquid mass. It gave on analysis the following numbers:—

	Found.	Calculated.
Carbon	18·15	18·69
Hydrogen	2·62	2·60
Oxygen	20·36	20·77
Oxide of lead	58·87	57·94

It is evident from these results, that by redissolving the dried compound, I had not succeeded in removing the whole excess of oxide of lead, but that in this salt the atomic relation of the carbon and hydrogen was likewise as 6 : 5. Admitting that the analysed salt contained 2 per cent. of oxide of lead, and deducting this, we obtain the following per-centage composition of the lead salt:—

Carbon	18·52	6	18·69
Hydrogen	2·67	5	2·60
Oxygen	20·78	5	20·77
Oxide of lead	58·03	1	57·94

With the remainder of the acid I prepared the silver salt in the following way:—The free acid was diluted with hot water, and mixed with an excess of still moist oxide of silver, which had been prepared by precipitating nitrate of silver with caustic potash and careful washing; the clear solution was filtered in a dark room, and evaporated as quickly as possible over sulphuric acid under the air-pump, at the same time carefully excluding the light. The salt effloresced, but only after nearly the whole of the water had been removed did it separate in a crystalline state; it is therefore easily soluble in water. Unfortunately I had so little of this compound at my disposal, that I did not venture to dry it in the air in order to determine the amount of water of crystallization. I feared that from the time it would require, decomposition might occur, which would render useless the elementary analysis, which was the principal object I had in view. And, in fact, this salt, which is of a beautiful white colour when it has been carefully protected from the light, very readily turns black even in daylight.

This salt dissolves in hot alcohol, but again separates almost entirely as the solution cools; it behaves therefore towards this solvent precisely like the silver salt of lactic acid prepared from milk or cane-sugar. According to Engelhardt and Maddrell's statement, however, the latter separates from the alcoholic solution in the form of a *crystalline* magma. I was never able to detect the least trace of crystallization in the silver salt of the acid prepared from flesh. It separates as a transparent gelatinous mass, even when a large quantity of alcohol has been used to dissolve it. Even after twenty-four hours I was only able to observe under the microscope some minute amorphous granules, but certainly no crystals.

When the salt is heated to 212°, it cakes together without exactly melting, and then readily acquires a dark colour; even at 176° it becomes somewhat yellowish, without being essentially decomposed, as will be seen from the following analysis. I was not able to deprive the salt entirely of its water under the air-pump; but on subsequently drying it at 176°, it lost nearly 1·5 per cent. in weight.

This salt therefore behaves in this respect like the corresponding one of lactic acid. The compound, dried at 176°, gave on analysis the following numbers:—

Carbon.....	18·26	6	18·28
Hydrogen.....	2·59	5	2·54
Oxygen.....	20·46	5	20·31
Oxide of silver.....	58·69	1	58·87

This salt therefore likewise contains 5 atoms of hydrogen to 6 atoms of carbon; and consequently the supposition, entertained at the commencement of this paper, that the difference between this acid and lactic acid might be attributable to a different amount of water, is not confirmed by these experiments, but is rather refuted; and Engelhardt's supposition, according to which the cause of this difference is attributable to the mono- and bibasic nature of the acids is considerably increased in probability. Unfortunately, want of material prevents me for the present from establishing this view. At all events, however, my experiments show that the two acids must be considered as isomeric compounds. That obtained from flesh may therefore be termed *paralactic* acid.—Poggendorff's *Annalen*, lxxv. p. 391.

On the Constituents of the Seed of Ivy. By Prof. L. Posselt.

An examination of the seed of *Hedera Helix* appeared interesting for several reasons. This plant belongs to a family which has no other representative in Europe; the seeds contain an unusually developed albumen, no starch and very little fat. This class of seeds has hitherto been very little examined; and it is scarcely known what substances act the part of these non-nitrogenous compounds. As in all seeds non-nitrogenous substances must be present along with the nitrogenous albumen, &c., and in the ivy the starch is wholly absent and no very large quantity of fat present, I concluded that it would contain some peculiar compounds to replace those in the germination. The taste of these seeds likewise indicates the presence of a peculiar substance, for it is excessively acrid, and produces in the larynx an exceedingly disagreeable sensation of dryness, which continues for a length of time. The fruit of this plant is a black berry of about the size of a pea; I have not submitted the fleshy part to minute examination, but it appears to me to consist principally of pectine, as it forms a stiff jelly even with a very large quantity of water. In this fleshy part are situated some seeds of the size of the *Semen Cynosbati*; they contain, as far as I have yet examined them,—1st, a nitrogenous substance resembling emulsine; 2nd, fat; 3rd, two peculiar acids; 4th, sugar; and lastly, some pectine and inorganic salts. Unfortunately my store of seed did not suffice to complete the investigation, which I hope to do by next summer.

The powdered fresh seeds were treated with æther to remove the fat; I thus obtained a green oil, which after being placed for some

days in a cool spot solidified. By pressure between folds of bibulous paper, I separated it into a liquid and a solid fat; the liquid oil proved to be oleine; it saponified very readily, and the lead salt prepared with it was soluble in æther; it was not further examined. To saponify the solid fat, it was necessary to melt it with hydrate of potash; when a clear solution had been prepared, it was purified by chloride of sodium, and then decomposed with tartaric acid. The fat so obtained solidified to a crystalline mass, and was of a dazzling white colour; it dissolved readily in hot alcohol, from which it crystallized in large, nacreous, snowy-white laminæ; it was purified by recrystallization until the melting-point remained constant at 86°; it could not be raised higher by further recrystallization. The acid was easily reduced to a powder, melted by the warmth of the hand, and decomposed carbonate of soda with effervescence. The soda salt, dissolved in absolute alcohol and precipitated with nitrate of silver, afforded a dazzling white salt, which became coloured by exposure to the light, and furnished the following results:—

I. 0·2500 grm. substance gave 0·0655 silver, corresponding to 27·4 Ag.

II. 0·4220 grm. substance gave 0·1160 silver, corresponding to 27·64 Ag.

It was impossible to make an elementary analysis from want of material. The constant melting-point and the appearance of the acid are in favour of its being a distinct fatty acid; it is, however, possible that it still contained oleic acid, which may have lowered the melting-point.

The seeds, which had been exhausted with æther, were now boiled with alcohol, and then separated from the alcohol by straining and pressure; this operation was repeated. The alcoholic solutions were then distilled. When the fourth part of the alcohol had passed over, a substance suddenly separated in a mass, which produced succussions and caused the liquid to run over; on cooling, an indistinct, crystalline, yellowish substance separated; it was impure *hederic acid*. As yet I have only accidentally succeeded in obtaining some perfectly pure in a flask which contained a mixture of an alcoholic solution of hederic acid with æther; the acid separated in a pure state. I was subsequently unable to obtain it again perfectly pure by this method. It has the following properties:—Its colour is a dazzling white; it crystallizes from alcohol in slender soft needles and laminæ; its alcoholic solution has a faint acid reaction; it is insoluble in water and in æther, and is precipitated by the latter from a concentrated alcoholic solution. It is void of smell, and possesses in a high degree the peculiar taste of the ivy seed. It combines with bases, forming neutral salts, and expels carbonic acid from its combinations. The salts cannot be obtained crystallized; they form gelatinous compounds, the majority of which are insoluble in water, but soluble in alcohol.

The salts of potash and ammonia are sparingly soluble in water, and separate after long standing in the form of gelatinous colourless precipitates. The lime and baryta salts are insoluble in water, but

soluble in boiling alcohol; they likewise form gelatinous masses, which dry to a white powder. The acid forms several combinations with oxide of lead, according to whether it is precipitated with a neutral or acid solution. The silver salt is white, and is obtained by precipitating an alcoholic solution of hederate of ammonia with nitrate of silver; it dissolves in alcohol, with which it may be boiled without decomposition; on cooling, it separates in a crystalline state. The pure acid contains 5·4 per cent. water of crystallization, which it parts with at 212°. It does not melt when heated, but diffuses a peculiar empyreumatic odour, and is entirely decomposed, leaving a residue of carbon. It dissolves in oil of vitriol, forming a splendid purple-red solution, which colour it retains for several days.

The pure acid, dried at 212°, gave on analysis—

Carbon	66·49	66·43
Hydrogen	9·50	9·41
Oxygen	24·01	24·16

I was unable to determine accurately the atomic weight of the acid, as the salts had been prepared from a not quite pure substance, and on that account furnished variable results.

The purification of the crude hederic acid is rendered difficult from the presence of a second new acid in the seeds, which, although differing considerably from the former in its properties, is nevertheless most tenaciously retained. I have not been able to obtain this acid in a pure state; the following however are the properties, as far as I am acquainted with them. It dissolves in water, alcohol and æther. I procured a concentrated solution of it in the following manner:—The seeds, exhausted with æther and alcohol, contain a large quantity of it; they were boiled with water, the solution acidified with acetic acid, and precipitated with an excess of basic acetate of lead; the precipitate was collected on a filter, and the clear solution mixed with ammonia, which precipitated the impure lead salt, which is of a beautiful sulphur colour; it was collected on a filter and washed, when it decreased in quantity; it was then formed with water into a paste and decomposed with sulphuretted hydrogen. The solution filtered from the sulphuret of lead contains the impure acid; it could not be crystallized by evaporation; the liquid became coloured from decomposition. Its aqueous solution is colourless, has an acid taste and reaction; it has no smell. This acid is well characterized by the following reactions:—Its combinations with the alkalies are soluble in water, and have a beautiful *yellow* colour, by means of which its presence may be readily detected; it is owing to it that the impure hederic acid dissolves in potash with a yellow colour, which the pure acid does not. It reduces silver and likewise the protoxide of mercury very readily when heated with solutions of these oxides. It furnishes a yellow precipitate with salts of baryta and lead; the same with chloride of calcium and ammonia, and corrosive sublimate and ammonia; it gives no precipitate with solution of gelatine, with protosulphate of iron or with persalts of iron; by the latter however it is coloured dark green. Sulphate of

copper furnishes a greenish precipitate. From the ease with which it is decomposed in the air and its reaction with persalts of iron, it appears to belong to the astringent substances. At all events, from the beautiful colour of its salts, it deserves further examination.—Liebig's *Annalen*, Jan. 1849.

Examination of the Liquid vomited during an attack of Cholera. *By* A. S. Taylor, F.R.S.

The fluid was vomited by a child, aged nine, who was suddenly seized with diarrhœa, followed by vomiting of the undigested remains of the breakfast, which had been taken more than three hours before the attack, and consisted of a mixture of gruel and arrowroot with bread. Collapse followed, the vomiting and diarrhœa continuing; there were no cramps; the dejections said to resemble soapy water. The case terminated fatally in fifty hours from the commencement.

The fluid examined was thrown up soon after the first vomiting of the undigested food. It was turbid, and when shaken resembled dirty water. When set aside, a curdy, insoluble white substance subsided. The only distinct traces of food were a few husks, resembling those of barley, undigested. Iodine did not colour either the sediment or the clear liquid blue. No blood was present. The white deposit had the appearance of pus, and was not ropy like mucus.

The supernatant liquid had the colour of diluted serum. Its specific gravity was 1·012. On evaporation it left a brown varnish-like layer of extract, which on incineration yielded an ash almost entirely soluble in water. The solution was slightly alkaline (alkaline carbonate), and was abundantly precipitated by nitrate of silver, the precipitate being insoluble in nitric acid; very slightly precipitated by a salt of baryta (sulphate of baryta). It did not contain a trace of a soluble phosphate, nor could any insoluble phosphate (of lime) be detected in the residue. The only alkali detected in the aqueous solution of the ash was soda. The proportion per cent. of animal matter and salts was—

Animal matter		2·5
Salts	Chloride of sodium in large proportion Sulphate of soda	0·8
Water		96·7
		100·0

The clear serous liquid was of a slightly acid reaction. No coagulation or turbidity was produced by ebullition, nor by strong nitric acid; nor was any opacity caused by ferrocyanide of potassium and acetic acid. Alcohol and pyrophosphoric acid also produced no change. It was therefore obvious that the liquid contained no albumen. Acetic acid produced no change; caseine and mucus, in a soluble or diffused form, were therefore absent. Neither muriatic nor nitric acid produced the reactions of the colouring matter of the bile. On ebullition with oxide of lead dissolved in caustic potash, it became

darker, indicating the presence of sulphur in the animal matter diffused through it. It was abundantly precipitated by the acetate of lead (from organic matter), most of the precipitate being redissolved by a small quantity of nitric acid; alum produced no change. Protonitrate of mercury produced a dense white precipitate in it; but there was no separation of oxide of mercury, as occurs when this salt is added to albumen, serum or gelatine. Bichloride of mercury produced a slight opacity. Tincture of galls produced an abundant white precipitate, not redissolved on ebullition. When mixed with solution of caustic potash in the cold, and acetic acid was added to the mixture, no precipitate was produced; the author has found that a precipitate has been uniformly produced on subjecting albuminous or serous liquids to this mode of testing.

The acidity of the liquid may have been due to the presence of some organic acid. The carbonate of soda in the ash was no doubt a product of the decomposition of the organic matter.

The *solid white deposit* was quite soluble in boiling caustic potash, and with lead gave indications of sulphur. The solution obtained by boiling the sediment in caustic potash was rendered opake by acetic acid, but excess did not render it clear. The alkaline solution was also precipitated by dilute nitric acid, and the precipitate was not redissolved by an excess of the acid. The white deposit was also soluble in boiling nitric acid, and the solution precipitated by dilution with water. Strong acetic acid did not cause it to swell up, nor was it dissolved on the addition of water and ebullition. It formed a reddish-purple solution with muriatic acid. Caustic potash did not render it gelatinous, as it does pus.

Hence albumen is not necessarily a constituent of the choleraic liquid; not a trace was present in this specimen. Fibrine was also absent. The animal substance existing in solution in the clear liquid differed from gelatine in containing sulphur and not gelatinizing. It may have consisted of bile altered by disease, or of some morbid animal product poured out by the blood under the influence of the choleraic poison.—*Abridged from Lond. Med. Gaz.*, Feb. 2, 1849.

On Asclepione. By Dr. C. List.

As is well known, *Asclepias syriaca* contains, especially at the flowering period, a white milky juice, which flows out in drops from the injured places. From the author's experiments on this substance, it consists of a peculiar crystalline body allied to the resins, and for which he proposes the name *Asclepione*.

This milky juice or latex is highly concentrated, thickish, has a slightly acid reaction, a somewhat acrid taste, and a faint smell like apricots. When heated, the albumen it contains coagulates, and encloses the particles of asclepione suspended in the juice so completely, that the liquid portion may be filtered perfectly clear. The asclepione is extracted from the coagulum by digestion with æther. After distilling off most of the æther, a perfectly clear solution remains, which on further evaporation solidifies to a crystalline mass.

However, the asclepione thus prepared is not pure; it contains a small quantity of another substance, which is left undissolved on repeated treatment with *anhydrous* æther.

Pure asclepione forms white, cauliflower-like, crystalline masses; on very slow evaporation it is obtained in concentric masses of radiated crystals; it is void of taste and smell, perfectly insoluble in water and alcohol, readily soluble in æther, less so in oil of turpentine, naphtha and concentrated acetic acid. It is not altered or dissolved by a strong hot solution of caustic potash. It is readily fusible, and then remains, like lactucone, amorphous and perfectly transparent. This amorphism renders the determination of the melting-point difficult; after repeated observations it was found to be 219°; when further heated it becomes yellow and is decomposed, giving off an odour resembling that of heated caoutchouc. It cannot be sublimed. The substance, dried at the ordinary temperature over sulphuric acid, gave—

Carbon.....	74·852	74·514	20	74·576
Hydrogen	10·767	10·452	17	10·532
Oxygen	14·381	15·034	3	14·892

Since, from its occurrence as well as from its properties, it appears to be most nearly allied to lactucone, the formula above given, supposing lactucone to be really $C^{40}H^{32}O^3$*, should perhaps be doubled, and its composition represented by $C^{40}H^{34}O^6$; it would then be isomeric with anhydrous camphoric acid. From want of material it was impossible to submit it to further experiment.—Liebig's *Annalen*, Jan. 1849.

On Tartrate of Strontia and Antimony, and on a Compound of the same with Nitrate of Strontia. By F. Kessler.

Tartrate of Strontia and Antimony, $SrO, SbO^3 + C^8H^4O^{10}$.—Hot saturated solutions of equivalents of tartar-emetic and nitrate of strontia when mixed furnish a crystalline precipitate, which is nearly insoluble in hot water, and which, when conveyed into a cold solution of nitrate of strontia and heated with it to nearly 212°, separates from this solution in minute prisms. These crystals, like the first precipitate, consist of the strontia-compound corresponding to tartar-emetic.

In this salt the tartaric acid is not so easily altered at a high temperature as in tartar-emetic and the corresponding baryta salt; the salt lost, by six hours' drying at 212°, $\frac{1}{4}$ per cent. in weight. It gave on analysis—

Strontia.....	15·26	1	15·43
Oxide of antimony	45·25	1	45·40
Tartaric acid	39·22	1	39·17

Tartrate of Strontia and Antimony with Nitrate of Strontia.—The solubility of the preceding salt in a solution of nitrate of strontia is owing to the formation of this double salt. It is obtained in beautiful large crystals when a solution of 1 part nitrate

* Chem. Gaz., vol. v. p. 75.

of strontia in 2 parts water is digested at a temperature between 86° F. and 95° for a length of time with an excess of the tartrate of strontia and oxide of antimony in the state of a very fine powder, and the solution then left at about 68° to spontaneous evaporation. The crystals dissolve readily in cold water; on heating the saturated solution, the tartrate of strontia and antimony separates in distinct crystals, which do not completely redissolve in the supernatant liquid after a long time, but only upon the addition of an excess of nitrate of strontia. When a crystal is placed in cold concentrated sulphuric acid, it is not altered; it is dissolved with effervescence when heated, with disengagement,—first, of carbonic oxide, without the solution becoming coloured; then nitric oxide; and lastly, sulphurous acid; and the liquid gradually assumes a brown colour. When heated, these crystals first lose water; then, without becoming black, burn like tinder, forming a porous mass, which continues to burn for some time.

This salt is the only known compound of a simple salt with a double salt. The author considers both the following formulæ as possible, but looks upon the second as most probable, although the numbers calculated according to the first agree better with the results found:—

	Found.	Calculated according to $SrO, SbO^3T, SrO\,NO^5 + 11HO$.	Calculated according to $SrO, SbO^3T, SrO\,NO^5 + 12HO$.
Strontia	19·13	19·19	18·87
Oxide of antimony	28·02	28·23	27·77
Tartaric acid	23·92	24·35	23·96
Nitric acid	..	9·96	9·80
Water.....	18·43	18·27	19·60

Poggendorff's *Annalen*, lxxv. p. 410.

Examination of the Oil of Imperatoria Ostruthium. *By* H. Hirzel.

The oil is obtained by distilling the plant with water; the stratum of oil floating on the water is separated and the water shaken with æther, as the oil is somewhat soluble in water. The oil is then rectified with a little water, and dried with chloride of calcium. It has then the following properties:—

It is a colourless, limpid, very mobile liquid, of aromatic odour and a burning taste; it burns readily with a bright smoky flame; begins to boil at 338°, but this gradually rises with the continued application of heat. The analysis of the oil, dried over chloride of calcium, gave—

Carbon	85·57	84·80	40	85·41
Hydrogen	11·45	11·38	33	11·74
Oxygen	2·98	3·82	1	2·85

As the boiling-point was not constant, the oil was submitted to a fractionated distillation. The portion which passed over between

338° and 374° had the same composition as the original oil. On the other hand, the portion which distilled over between 392° and 428° differed considerably from the pure oil. It possessed a more disagreeable, somewhat empyreumatic odour, a slightly yellowish colour, and was thicker. It had the following composition:—

Carbon	81·74	30	81·08
Hydrogen	11·27	26	11·71
Oxygen	6·99	2	7·21

On distilling the oil with anhydrous phosphoric acid, a perfectly transparent colourless liquid was obtained, which had an aromatic taste and an odour resembling rosemary; it possessed the following composition:—

Carbon	87·76	10	88·23
Hydrogen	11·76	8	11·77

This hydrocarbon forms a compound with muriatic acid, which is prepared by passing pure muriatic gas into the oil until no more is absorbed; a reddish-yellow liquid is obtained, which is purified by distillation with water, and deprived of water by means of chloride of calcium. In the pure state it forms a liquid of agreeable odour and aromatic taste, with the following composition:—

Carbon	74·98	30	75·00
Hydrogen	10·86	25	10·42
Chlorine.....	13·28	1	14·58

Chlorine is absorbed by the oil with considerable evolution of heat and separation of muriatic acid gas. It forms a yellow, thick, oily liquid, which is heavier than water, has a peculiar smell and an acrid taste. It behaves in the same manner towards bromine. On comparing the oil of *Imperatoria* with the other essential oils, it is found to exhibit considerable analogy with those isomeric essential oils possessing the formula $C^{10}H^8$; and it is therefore highly probable that it likewise is isomeric with those oils. On this supposition the compound with muriatic acid is $3(C^{10}H^8) + HCl$. This view is further supported by its application to the essential oil; for the rational formula $4(C^{10}H^8)+HO$ and $3(C^{10}H^8)+2HO$ may readily be derived from the empirical formulæ $C^{40}H^{33}O$ and $C^{30}H^{26}O^2$.

All these compounds would consequently be derived from the same hydrocarbon, and the oil of *Imperatoria* would be a mixture of different hydrates and the same hydrocarbon ($C^{10}H^8$). This also readily explains the action of anhydrous phosphoric acid upon the oil; it deprives it of its water of hydration, and separates the pure hydrocarbon. The author therefore includes the oil of *Imperatoria* in the series of the terebens, which differ only in their different capacity of saturation, as follows:—

Muriate of the oil of lemons.....	=	$(C^{10}H^8)+HCl$
„ „ turpentine	=	$2(C^{10}H^8)+HCl$
„ „ *Imperatoria*	=	$3(C^{10}H^8)+HCl$
„ „ Neroli.....	=	$3(C^{10}H^8)+2HCl$

Pharm. Cent. Blatt., Jan. 17, 1849.

Analysis of Lymph. *By* M. Geiger.

The author had an opportunity of examining the lymph from the lymphatic vessels of the foot of a horse, under the direction of Dr. Schlossberger. It was collected from a small crack beneath the fetlock of the hind-foot.

The drops of fluid, which flowed out with varying rapidity, were clear like water, and singly almost colourless; in greater quantity, of a slightly yellowish colour, of a disagreeable smell and a slightly salt taste. The specific gravity at a mean temperature was 1017. Immediately after it had flowed out, a colourless gelatinous coagulum formed in it, which in the course of a few hours adhered together and floated on the surface. The subnatant liquid was perfectly clear, slightly yellowish, and exhibited under the microscope but very few globules.

It gave no reaction with test-papers. The serum scarcely became clouded on its being heated, and even after being boiled for ten minutes only a few flakes of albumen were thrown down; but when a few drops of acetic acid were added to the boiling fluid a considerable precipitate was obtained. This however did not take place on adding it to the cold liquid. An addition of rennet (calf's stomach) and milk-sugar scarcely troubled the liquid. When the serum was evaporated, a film was formed, which was renewed when removed. On incinerating the residue, an ash was obtained, which strongly effervesced with acids, and contained carbonic, phosphoric, sulphuric and hydrochloric acids, combined with potash, soda, lime and a trace of oxide of iron.

The fresh lymph, treated with potash, even in the cold, showed the presence of ammonia. Carbonic acid could not be satisfactorily detected by the addition of other acids to the fresh lymph. The following is the result of its analysis:—

Water	983·7
Fibrine	0·4
Albumen	6·2
Extractive matter	2·7
Fixed salts	7·0

Together with traces of fat and of salts of ammonia.

Schlossberger has added some observations to this paper, which tend to throw considerable light on the nature of this fluid, about which so much is said and so little in reality known.

He first shows the purity of the lymph by the statement of the veterinary surgeon, by the white coagulum of fibrine, and by its behaviour under the microscope, by which he was able to distinguish globules of different sizes and form, the largest of which were smaller than blood-globules, evidently granulated, with sharp edges, and often with a visible nucleus; some were round and some elliptical. The smallest of them, in which no nuclei could be discovered, perfectly resembled the isolated nuclei. Both varieties were perfectly insoluble in æther. Neither blood-globules nor fat-globules could be detected.

The time of coagulation varied very much, from four to eighteen minutes after the discharge of the fluid. At first the coagulum had a jelly-like transparency; afterwards it contracted considerably, and became opake and more consistent. It never assumed a red tinge in the air. Schlossberger also mentions, as remarkable, the behaviour of the albumen on heating the liquid, which was perfectly neutral. Although *free*, alkalies are not necessary to impart to albumen many of the properties of caseine, for it exhibits these characters when simply combined with soda; still it is probable that the presence of ammoniacal salts, which often react acid, had masked the alkaline reaction of the albuminate of soda. The lymph serum was not coagulated by æther.

In some experiments which Schlossberger made with the horse, by adding several salts to its drink, and among others ferrocyanide of potassium, he only obtained a negative result, even after two hours.

The quantity of lymph which flowed from the horse daily amounted to from 3 to 5 lbs. It suffered from this for several years, but did not appear to waste, although it lost strength.—*Arch. für Phys. und Heilkunde Jahr.* lv. p. 391, as inserted in the *Dublin Quarterly Journal of Medical Science*, Feb. 1849.

On the Occurrence of Sugar in the Liver.
By C. L. Bernard *and* C. H. Barreswil.

The authors exhibited to the French Academy a sample of alcohol which they had prepared by fermenting sugar obtained from the liver. According to numerous experiments, the sugar exists only in the tissues of the liver, and in no other organ. Even in those animals which do not take any saccharine or amylaceous food, sugar was found in the liver; so that its occurrence there does not appear to depend on the food.—*Comptes Rendus*, xxvii. p. 514.

On some Double Salts of the Cyanide of Mercury. By H. Custer.

Cyanide of Mercury and Iodide of Sodium, $2HgCy + NaI + 4HO$, is obtained when 100 parts of cyanide of mercury and 58·65 parts of iodide of sodium are dissolved, mixed, and the solution crystallized. When crystallized from water, it forms minute, colourless, transparent, silky, four-sided prisms; from alcohol it separates in quadratic plates. Even after a considerable length of time it is only altered superficially, becoming yellowish. If the solution of this double salt is long exposed to the air, the soda absorbs some carbonic acid; no hydriodic acid however is eliminated, but the iodine combines with some mercury to form periodide of mercury, which remains dissolved, and colours the liquid yellowish, whilst a corresponding quantity of prussic acid is set free.

When the salt is heated to 320° it becomes yellowish, and at 410° periodide of mercury is given off. Heated still further, the crystals are entirely decomposed with violent decrepitation, some prussic acid

is given off, a little periodide of mercury, but principally cyanogen and mercury; and the residue is rendered black by paracyanogen. At a still higher temperature some iodine is given off; and there is left after a faint ignition, iodide of sodium mixed with carbon, some soda and traces of cyanide of sodium.

The double salt does not part with any water of crystallization at 212°; a little escapes at 302°, and the whole at 410°; but at this temperature some periodide of mercury also sublimes. It dissolves in 4½ parts of water at 64°, and in six-sevenths of boiling water forming a colourless solution; of alcohol of 0·833 spec. grav. it requires for solution 6½ parts at the ordinary temperature, and 2 parts on boiling. Sulphuric, nitric and muriatic acids precipitate periodide of mercury from the double salt, with elimination of prussic acid; in a very large excess of the two last acids the precipitate entirely redissolves. This salt gave on analysis—

Cyanide of mercury ..	57·97	57·86	57·68	2	=3189·1	57·88
Iodide of sodium	34·45	34·26	..	1	1870·4	33·95
Water.....	8·40	8·33	..	4	450·0	8·17

Cyanide of Mercury and Iodide of Barium, $2HgCy + BaI + 4HO$, is prepared in the same manner as the preceding salt, using iodide of barium. It crystallizes in thin quadratic prisms, which are transparent, colourless, have a strong nacreous lustre, and are fatty to the touch. On long exposure to the air, this salt absorbs a considerable quantity of water without altering its form, but becomes reddish. This decomposition takes place slowly even in a closed, but not perfectly full vessel. On recrystallizing the crystals, a red stain was formed at the upper margin of the dish. This decomposition proceeds more rapidly when the salt is in an aqueous or alcoholic solution, as on boiling there is each time a more copious flocculent precipitate of carbonate of baryta, and the solution becomes proportionately coloured. When evaporated slowly to dryness over sulphuric acid, the salt forms thick quadratic prisms, which are turbid and milk-white; they inclose minute quantities of carbonate of baryta, and also some minute scattered crystals of periodide of mercury. This double salt behaves precisely like the preceding one when exposed to an elevated temperature; the last portion of water of crystallization is given off at 410°, with traces of periodide of mercury. After a strong heat, brown iodide of barium is left, with a trace of cyanide of barium, which dissolves almost entirely in water. The salt dissolves in 16½ parts of water at 64°, and in two-fifths boiling water, forming a colourless solution; in 22½ parts of alcohol of 0·833 at the ordinary temperature, and in 1⅔ boiling alcohol, with a yellow colour. The boiling saturated aqueous and alcoholic solutions very nearly solidify on cooling. Towards muriatic and nitric acids the salt behaves like the preceding one; sulphuric acid precipitates sulphate of baryta and iodide of mercury, which latter redissolves in a large excess of muriatic acid. Caustic potash, carbonate of potash and ammonia precipitate the baryta; caustic ammonia furnishes no precipitate. Analysis gave—

Cyanide of mercury.....	52·80	52·30	2=3189·1		52·48
Iodide of barium	39·63	39·87	1	2437·5	40·11
Water	6·86	7·30	4	450·0	7·40

Cyanide of Mercury and Iodide of Strontium, 2HgCy + SrI + 6HO, is prepared with iodide of strontium in the same manner as the preceding salts; it crystallizes in thin quadratic prisms, like the baryta salt; is less easily altered by exposure to the air, but is also partially reddened, and carbonate of strontia gradually separates from the solution. The strontia salt is more readily decomposed by heat than the salt of barium; between 212° and 220° it parts with about two-fifths of its water of crystallization; at 302° the whole mass is coloured faintly yellow, and traces of periodide of mercury are deposited in the upper part of the tube; at 356° this film is more distinct, and the odour of prussic acid is perceptible, while some water still escapes from the salt. When heated to redness, it leaves iodide of strontium, with traces of cyanide of strontium, which dissolves in water with the exception of a mere trace.

This salt dissolves in 7 parts of water at 64°, in one-third part of boiling water; in 4 parts of alcohol of 0·833 at 64°, and five-sixths of boiling alcohol. In this case the alcoholic solution is yellowish, and the aqueous one colourless. Analysis gave—

Cyanide of mercury.....	53·21	53·71	2=3189·1		53·23
Iodide of strontium	36·15	35·58	1	2126·8	35·50
Water	10·85	11·04	6	675·0	11·27

Cyanide of Mercury and Bromide of Calcium, 2HgCy + CaBr + 5HO, is prepared with bromide of calcium in the same manner as the preceding salts, and forms colourless, transparent, very shining, oblique, quadrilateral prisms, which are but very little coloured under the influence of light and humidity, and when preserved in closed vessels remain unaltered. The solution in water is neutral, and when exposed for a long time to the air deposits some carbonate of lime.

At 410° this salt still remains white, and gives off but mere traces of perbromide of mercury; at a higher temperature it is decomposed. The residue dissolves in water, forming a clear solution, and still has a neutral reaction. At a higher temperature and towards reagents this salt behaves like the preceding ones. Oxalic acid precipitates the lime; it dissolves in about equal parts of water at 64°, and in not quite one-fourth part of boiling water; it requires 2 parts of alcohol of 0·833, and not quite 1 part at a boiling temperature. The boiling, saturated, aqueous and alcoholic solutions solidify on cooling nearly to one mass of crystals. On analysis it gave—

Cyanide of mercury.....	66·72	65·74	2=3189·1		63·96
Bromide of calcium.....	21·96	22·00	1	1234·3	24·75
Water	11·22	11·21	5	562·5	11·29

Cyanide of Mercury and Acetate of Soda.—The two salts, dissolved in equivalent proportions, afforded, on evaporating the mixed

solutions, crystals of cyanide of mercury, and then crystals of both salts at the same time; subsequently some crystals separated from the mother-liquor, which were a double compound; they could be recrystallized without any change of form. On analysis they gave—

Cyanide of mercury.....	45·00	1 =	46·72
Acetate of soda.....	31·71	1	30·22
Water	22·56	7	23·06

This result could not be again obtained on trying to prepare them a second time. The author therefore leaves it undecided whether in the present instance the two salts crystallized accidentally in this proportion, or whether a definite compound was produced.

Numerous other experiments were made to combine oxysalts with cyanide of mercury, but with negative results. The author is therefore inclined to believe that under ordinary circumstances no such salts are produced.—*Archiv der Pharm.*, lvi. p. 1.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Preparation of Vitrifiable Pigments. By A. Wæchter.

[Continued from p. 68.]

Yellow Pigments for painting upon Porcelain.

The yellow vitrifiable pigments are lead glasses, coloured either by antimonic acid or oxide of uranium. The antimoniate of potash is prepared by igniting 1 part of finely-powdered metallic antimony with 2 parts of nitre in a red-hot Hessian crucible, and washing the residue with water. The oxide of uranium is obtained in the fittest state by heating the nitrate until the whole of the nitric acid is expelled.

Lemon-Yellow.

8 parts antimoniate of potash, $2\frac{1}{2}$ parts oxide of zinc, 36 parts of lead glass (prepared by fusing together 5 parts minium, 2 parts of white sand and 1 part of calcined borax), are intimately mixed and heated to redness in a porcelain crucible, which is placed in a Hessian crucible, until the mixture forms a paste; it is then taken out with a spatula, pounded after cooling, and ground upon a plate of glass. If the pigment is fused longer than requisite for the perfect union of the ingredients, the yellow colour is converted into a dirty gray by the destruction of the antimoniate of lead.

Light Yellow.

4 parts antimoniate of potash, 1 part oxide of zinc and 36 parts of lead glass (prepared by fusing together 8 parts of minium and 1 part of white sand) are well mixed, fused in a Hessian crucible, and after cooling pounded and ground. In the preparation of this

colour, long fusion is less injurious than with the preceding one, owing to the absence of the borate of soda in the lead glass. The colour itself is more intensely yellow than the preceding one, and is extremely well-adapted for mixing with red and brown pigments; but it does not furnish such pure tints as that when mixed with green; owing to its higher specific gravity, it flows more freely from the brush, and may be laid on in a thicker layer without scaling off after the firing.

Dark Yellow, I.

48 parts minium, 16 parts sand, 8 calcined borax, 16 antimoniate of potash, 4 oxide of zinc and 5 parts peroxide of iron (*caput mortuum*) are intimately mixed and fused in a Hessian crucible until the ingredients have perfectly combined, but no longer; otherwise the golden-yellow colour is converted into a dirty gray, as in the case of the lemon-yellow pigment.

Dark Yellow, II.

20 parts minium, $2\frac{1}{2}$ white sand, $4\frac{1}{2}$ antimoniate of potash, 1 part peroxide of iron (*caput mortuum*) and 1 part oxide of zinc are well mixed and fused in a Hessian crucible. Long fusion is less injurious in this case than in the preceding. Iron-red pigment may be laid on and near this dark yellow II. without its being destroyed or the harmony of the tints injuriously affected.

For landscape and figure painting the above-mentioned yellow pigments should be made less readily fusible, in order to paint with them upon or beneath other colours, without any fear of what has been painted being dissolved by the subjacent or superposed pigment. This property is given to it by the addition of Naples yellow, which is best prepared for this purpose by long-continued ignition of a mixture of 1 part tartar-emetic, 2 parts nitrate of lead, 4 parts of dry chloride of sodium, in a Hessian crucible, and washing the pounded residue with water. Very useful yellow colours are likewise obtained by mixing this Naples yellow with lead glass; they are, however, more expensive than those above given. A very excellent yellow for landscape painting may be prepared, for instance, by mixing 8 parts Naples yellow and 6 parts lead glass (obtained by fusing 2 parts of minium with 1 of white sand and 1 of calcined borax).

The yellow pigments obtained with antimony, after being burnt-in upon the porcelain, appear under the microscope to be mixtures of a yellow transparent substance (antimoniate of lead?) and a colourless glass, and not homogeneous yellow glasses.

Uranium-Yellow.

1 part oxide of uranium, 4 parts lead glass (prepared by fusing 8 parts minium with 1 part white sand), are intimately mixed and ground upon a glass plate. This colour is not adapted for mixing with others, with which it produces discordant tints. It may be shaded with dark purple or violet.

Uranium-Orange.

2 parts oxide of uranium, 1 part chloride of silver and 3 parts bismuth glass (prepared by fusing 4 parts of oxide of bismuth with 1 part of crystallized boracic acid) are intimately mixed and ground upon a plate of glass. This orange is not adapted, any more than the yellow pigment, for being mixed with other colours. When examined under the microscope, after being burnt-in upon porcelain, the uranium pigments appear as pale yellow-coloured glasses, in which unaltered oxide of uranium is suspended. Only a small portion therefore of the oxide of uranium has dissolved in the fusing.

Green Pigments for painting upon Porcelain.

Blue-Green.

10 parts of the chromate of protoxide of mercury and 1 part of chemically-pure oxide of cobalt are ground upon a glass plate in order to produce as intimate a mixture as possible; the mixture is then heated in a porcelain tube, open at both ends, until the whole of the mercury is expelled. The beautiful bluish-green powder thus obtained is then transferred into a porcelain crucible, and the lid cemented to it with glaze. The full crucible is exposed to the highest temperature of the porcelain furnace during one firing, the crucible carefully broken after the cooling, and the pigment washed with water to remove a small quantity of chromate of potash. In this manner a compound of oxide of chromium and oxide of cobalt is obtained in nearly equivalent proportions, which possesses the bluish-green colour of verdigris.

The blue-green pigment consists of a mixture of 1 part of the above compound of oxide of chromium and oxide of cobalt, $\frac{1}{2}$ part of oxide of zinc, and 5 parts of lead glass (prepared by fusing together 2 parts minium, 1 part white sand and 1 part calcined borax), which are mixed and ground upon the glass plate. By mixing this blue-green with lemon-yellow, any desired intermediate tint may be produced. 1 part of blue-green to 6 parts of lemon-yellow furnishes a beautiful grass-green.

Dark Green.

The chromate of mercury is treated separately in the same way as the mixture of it with oxide of cobalt for the blue-green; and 1 part of the beautiful green oxide of chromium thus obtained is mixed with 3 parts of the same lead glass as given under blue-green, and ground upon the glass plate.

Green for shading.

8 parts chromate of mercury and 1 part oxide of cobalt are intimately mixed, and exposed in a shallow dish to the strongest heat of the porcelain furnace during one of the bakings. In this manner a compound of oxide of chromium and oxide of cobalt is obtained, of a greenish-black colour, which, mixed with twice the weight of the lead glass directed for the blue-green, furnishes a very infusible blackish-green colour for shading other green colours.

When thin splinters of the green pigments of chromium, burnt-in upon porcelain, are examined under the microscope, it is distinctly seen that particles of the oxide of chromium or of the oxide of chromium and cobalt are suspended undissolved in the colourless lead glass.

Blue Pigments for painting upon Porcelain.

Dark Blue.

1 part chemically-pure oxide of cobalt, 1 part oxide of zinc, 1 part lead glass (prepared by fusing together 2 parts of minium, 1 sand and 1 calcined borax) and 4 parts of lead glass (prepared by fusing together 2 parts of minium and 1 of white sand) are well mixed and fused in a porcelain crucible, for at least three hours, at a red heat: then poured out, reduced to powder, and ground upon the glass. When this pigment cools slowly, it solidifies to a mass of acicular crystals. Long-continued fusion at not too high a temperature is requisite to obtain a beautiful tint; this is best attained by fusing it during one of the bakings in the second floor of the porcelain furnace; this is also the cheapest and best way of fusing the lead glasses.

Light Blue.

1 part oxide of cobalt, 2 parts oxide of zinc, 6 parts lead glass (prepared by fusing together 2 parts of minium and 1 of white sand) and $1\frac{1}{2}$ part lead glass (prepared by fusing together 2 parts of minium, 1 part white sand and 1 part calcined borax) are well mixed and fused as directed for the dark blue.

Blue for shading.

10 parts oxide of cobalt, 9 parts oxide of zinc, 25 parts of lead glass (obtained by fusing 2 parts of minium and 1 of white sand) and 5 parts of lead glass (prepared by fusing together 2 parts of minium, 1 part of white sand and 1 part calcined borax) are mixed and fused as directed for the dark blue. The colour is only used for shading, or to be applied upon or beneath the two preceding blue pigments, for which purpose it is admirably suited from its being very difficult of fusion.

Sky-Blue.

2 parts of dark blue, 1 part oxide of zinc, and 4 parts of lead glass (prepared by fusing 4 parts minium with 1 of white sand) are intimately mixed and ground upon the glass plate. This pigment is employed either alone or mixed with other colours only for painting the sky in landscapes.

The blue pigments described likewise appear under the microscope, after having been burnt-in upon the porcelain, not to be homogeneous blue glasses, but mixtures of a transparent blue substance (silicate of cobalt and zinc?) and a colourless glass.

Turquoise-Blue.

3 parts of chemically-pure oxide of cobalt and 1 part of pure oxide of zinc were dissolved together in sulphuric acid, then an

aqueous solution of 40 parts ammonia-alum added, the mixed solutions evaporated to dryness, and the residue heated to expel the whole of the water, then reduced to a powder and exposed in a crucible to an intense red heat for several hours. The colour is most beautiful when it has been exposed during one firing to the heat of the porcelain furnace. It is a combination of nearly 4 equivs. alumina, 3 equivs. oxide of cobalt and 1 equiv. oxide of zinc, and is of a beautiful turquoise-blue colour. When the oxides are mixed in other proportions than those above given, they do not furnish such beautiful coloured compounds. To impart to it a slightly greenish tint, a little moist recently-precipitated protochromate of mercury is mixed with the above-described solution of ammonia-alum, zinc and cobalt; with the above quantities, one-sixteenth part of the chromate, calculated in the dry state, suffices.

The turquoise-blue vitrifiable pigment is prepared by mixing 1 part of the compound of alumina, oxide of zinc and cobalt with 2 parts of bismuth glass (prepared by fusing 5 parts of oxide of bismuth with 1 part of crystallized boracic acid).

The recipe for the preparation of the turquoise-blue pigment, communicated in the 'Traité des Arts Céramiques' by Brongniart, is incorrect; for a lead glass of the composition there given (3 parts of minium, 1 part sand, 1 part boracic acid) destroys the turquoise-blue pigment entirely on fusion, and only a dirty bluish-gray colour is produced. On examining under the microscope the turquoise-blue pigment burnt-in upon porcelain, it appears to be a mixture of a transparent blue substance and a colourless glass. The transparent blue substance in all probability is the above-described compound of oxide of cobalt and alumina, which is of itself transparent under the microscope, but the transparency of which is increased by the surrounding fused glass of bismuth, just like the fibres of paper by oil. This is probably the case also with the microscopic blue constituent of the other blue vitrifiable pigments, and which is probably silicate of zinc and cobalt; for this, when prepared separately, forms a pure blue transparent powder.

[To be continued.]

Ink for Steel Pens. By M. Runge.

A most excellent ink for steel pens is obtained by exhausting 10 parts of logwood with a sufficient quantity of boiling water to obtain 80 parts of liquid. To 1000 parts of this decoction is now gradually added 1 part of *yellow* chromate of potash, when the liquid turns first reddish-brown, and finally bluish-black. No gum or any other additions are requisite; on the contrary, they are injurious. This liquid is an actual solution, which may be filtered; no deposit is formed in it, and the writing is not removed by immersing the paper in water.—Dingler's *Polyt. Journ.*, cix. p. 227.

THE CHEMICAL GAZETTE.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

Observations on Caffeine. By Dr. F. Rochleder.

In works on chemistry we find it stated that caffeine is not altered by chlorine nor nitric acid. Stenhouse first showed that a crystalline substance, which he called *nitrotheine*, was produced by the action of nitric acid upon caffeine. In his paper he enumerates the results he obtained in the analysis of this body, but does not propose any formula for it. At the same time Dr. Stenhouse observes that under certain circumstances the caffeine is converted by nitric acid into a substance which assumes with ammonia the colour of murexide. I have completely confirmed these statements of Dr. Stenhouse. When caffeine is treated with nitric acid, various products originate, according to the concentration of the acid, the length of the action and the temperature employed; the examination of these products would probably lead to as interesting a series of results as those furnished by the metamorphosis of uric acid. After having assured myself that the substance which assumes the colour of murexide is also produced by the action of chlorine, a mixture of chlorate of potash and muriatic acid, nitromuriatic acid, &c., I deemed it advisable to examine more accurately the reaction which occurs, as it was to be hoped that a product obtained through the means of such various oxidizing agents would allow of some conclusion being drawn as to the constitution of caffeine.

It was at first necessary to discover a more certain and productive method of preparing this substance, and to examine whether it was the only product of the action of oxidizing agents upon caffeine. From the circumstance that the platino-chloride of caffeine dissolves in hot nitric acid with a reddish-yellow colour and evolution of nitrous vapours, and that this liquid on cooling deposits a platinum salt in scaly crystals, which are no longer platino-chloride of caffeine, it seemed probable that along with other substances a basic product is formed, which contains a part of the nitrogen of the caffeine. After many experiments, I found the following method best adapted for the preparation of this product. Caffeine is dissolved in boiling water; the saturated solution solidifies on cooling to a mass of crystals. By stirring with a glass rod a thick paste is obtained, into which chlorine gas is passed until the whole of the caffeine is decomposed; this is ascertained from a drop of the liquid, treated

with chlorine, on being mixed with a drop of caustic potash of 1·27 spec. grav., immediately giving a white precipitate when any undecomposed caffeine is present. Under the microscope this precipitate appears as a mass of matted silky needles.

As soon as all the caffeine is decomposed, no more chlorine is passed through it. During the operation the caffeine gradually disappears, owing partly to decomposition and partly to the formation of muriatic acid. When the whole of the caffeine has disappeared, about a third is decomposed, while the remainder is dissolved as muriate of caffeine.

Whilst caffeine may be mixed with the strongest solution of caustic potash at the ordinary temperature without experiencing any decomposition, the liquid obtained by passing chlorine through the paste of caffeine gives off so large a quantity of ammonia upon the addition of solution of potash after saturating the muriatic acid, that one would almost believe the solution to be one of chloride of ammonium. This liquid produces, after some time, a purple colour upon the skin, just like a solution of alloxan. The liquid acquires a splendid indigo-blue colour upon the addition of protosulphate of iron and an alkali. When this liquid is evaporated in the water-bath, a large quantity of muriatic acid is given off. At the margin of the liquid the residue formed by evaporation is coloured yellow, in consequence of incipient decomposition. To prevent this, the liquid is constantly stirred. When it has acquired a certain degree of concentration, crystals begin to form, the quantity of which goes on increasing. When the liquid has attained a syrupy consistence, the crystals are removed with a platinum spatula, and laid upon blotting-paper to absorb the mother-liquor adherent to them. The mother-liquor is evaporated to the consistence of honey, set aside to cool, mixed with some cold water, and stirred with a glass rod, when more of the crystals separate, which are collected upon a filter and washed with water, in which they are very sparingly soluble.

The stirring the liquid with a glass rod during the evaporation greatly facilitates the separation of the crystals, which are frequently not formed when it is omitted, even when the liquid is evaporated to the consistence of honey. They are then formed when, after the addition of some cold water, the thick liquid is rubbed against the sides of the vessel with an angular glass rod at those points where the sides have come in contact with the rod.

The liquid from which these crystals have subsided contains another substance of basic nature, the presence of which is readily detected by chloride of platinum. When the mother-liquor from the crystals is mixed with some water and then with chloride of platinum, a copious precipitate of a double salt falls, which is of a light yellow colour when precipitated from dilute, and of a dark yellow when thrown down from concentrated liquids. The salt is tolerably soluble in cold, and readily soluble in hot water. The solution is of a dark reddish-yellow colour, and deposits on slow evaporation crystals which resemble the bichromate of potash.

The above-mentioned crystallized body constitutes, as to quantity,

the principal product of the decomposition. It forms a mass of granular crystals, having a remarkable resemblance to alloxantine, with which it likewise agrees in its behaviour towards several reagents. It dissolves with difficulty in cold, more readily in hot water. From the hot saturated solution only a portion of the quantity dissolved is deposited on cooling; the greater portion remains in solution. When this solution is stirred and the rod rubbed against the sides of the vessel, the liquid becomes turbid, and deposits the greater part of the substance in the state of a fine crystalline powder.

In an atmosphere of ammonia the white crystals first become rose-red to dark purple; a piece of paper saturated with a solution of this substance, becomes of a brilliant red in the air; and this colour is so permanent that it has kept for a year unaltered. This liquid likewise produces red stains upon the skin, which cannot be washed out by means of water, exactly resembling a solution of alloxan. When moistened with caustic potash, the substance is coloured dark violet; but the compound is not very stable, for in a few seconds the colour entirely disappears, with a copious evolution of ammonia. If the crystals are mixed with a paste of hydrate of baryta, instead of with a solution of potash, a splendid violet-blue compound is produced, which in a very short time loses its colour, as is the case with alloxantine. A protosalt of iron and an alkali added to a solution of this substance colour it of a beautiful indigo-blue. Nitrate of silver is instantly decomposed by this substance, metallic silver being separated in black flakes. A solution of chloride of platinum is not altered even on the application of heat.

When this body is heated, it behaves exactly like alloxantine; it first turns yellow, then brownish-yellow, and now dissolves in water with a purple colour. When its aqueous solution is evaporated, it is left in the form of a yellowish varnish upon the vessel, is coloured reddish-yellow on being carefully heated, and dissolves in an aqueous solution of ammonia with the colour of murexide. It is however impossible to obtain crystals of murexide from this solution. On dry distillation we obtain a crystalline sublimate and a red amorphous substance, which is formed by a portion of the substance volatilized without decomposition being changed by the ammonia produced in the decomposition of another portion. When the substance is thrown upon hydrate of potash in a state of fusion, copious purple vapours are disengaged, formed by a portion of the substance being volatilized undecomposed before the hydrate of potash can act upon it; whilst the layer of substance in contact with the hydrate of potash is decomposed with evolution of ammonia, which colours the vapours of the portion sublimed in the undecomposed state.—Liebig's *Annalen*, Jan. 184[illegible]

On the Changes which the Egg undergoes during its Incubation.

Seraf. Cappezuoli* has instituted some experiments to determine the quantity and quality of the substances assimilated during the

* Polli's Annali di Chimica, Dec. 1846.

development of the egg, and immediately after the chick is disengaged from the shell. His results are as follows:—

1. During the incubation and the first few days of the existence of the chick, after leaving the shell, the quantity of fat does not diminish so rapidly as the albuminous substances.

2. During the incubation, the total diminution is very small, but becomes remarkable if the chick is left without food for some time after its expulsion from the shell.

3. Chickens fed on starch only exhibit a diminution of their fat; and even when fed in the ordinary manner, a considerable diminution of fat and of albuminous substance is perceptible; from which it may be concluded that the animal consumes more in the first days of its existence than it assimilates.

Baudrimont and Martin Saint-Ange* have published a very important and complete investigation of the chemical appearances and changes which the egg presents during its incubation, from which the following results may be deduced:—

1. Eggs diminish in weight during their incubation, as was already well-known.

2. Atmospheric air containing a certain amount of moisture and a moderate temperature are absolutely necessary.

3. They absorb oxygen, and at the same time evolve water, carbonic acid, nitrogen and some sulphur-compound, not further known.

4. The loss of weight sustained by the eggs is always smaller than the sum of the water, carbonic acid and nitrogen expired; it is even smaller when the carbonic acid is reckoned as carbon, which shows that the oxygen of this acid is derived from the air.

5. The oxygen necessary during incubation is partially absorbed and partially employed in the formation of water and carbonic acid.

6. The volume of absorbed oxygen is exactly equal to that contained in the evolved carbonic acid; and the volume of evolved nitrogen is about one-half of the latter, or about a fourth part of the oxygen absorbed.

7. The fatty bodies are diminished in the egg during the time of incubation, and at the same time the nitrogenous substances are altered in constitution, as is easily seen by the evolution of nitrogen.

8. The absorbed oxygen and the expired carbon and nitrogen stand in definite proportions to one another, and can be expressed by the following formula:—$8O+2C+N$, which gives $4O+2CO^2+N$. If the oxygen were partially employed in the formation of water, we should have $4HO+CO^2+N$, of which H^4C^2N would have been derived from the egg.

9. The incubated is richer in oxygen than the fresh egg.

10. The inorganic elements change considerably in their nature and relative proportions, as well as in physical characters.

11. The phænomena attending the development of the embryo exhibit a perfect example of nutrition, in which the nutriment is not

* Recherches sur les Phénomènes Chimiques de l'Evolution embryonaire des Oiseaux et des Batraciens; Annal. de Chim. et de Phys., Oct. and Nov. 1847.

assimilated until it has been exposed to the action of oxygen.—From Mr. W. Sullivan's Retrospect of the Progress of Chemistry in the *Dublin Quarterly Journal of Medical Science*, Feb. 1849.

Chemical Examination and Analysis of a peculiar Fatty Matter contained in an Ovarian Cyst. By Thornton J. Herapath*.

Physical Characters.—A yellowish-white, granulated, unctuous substance, having numerous hairs intermixed. It possessed a fœtid sour smell; it floated on water; a few pus-globules only washed out of it. Its appearance was not unlike stale clotted Devonshire cream. When placed in water somewhat below 98° F., it was partially melted, and then had the consistence and smell of toasted cheese. It was still opake.

The hairs were separated from the fat by enclosing the whole in a muslin bag, and immersing this in boiling water, when pressure forced the liquid fat through the pores of the muslin, and the hairs remained in the bag. These were subsequently washed with æther.

The hairs were curly, and light brownish-red in colour. Some were half white. Some had bulbous expansions, others were destitute of them; all were pointed at one extremity, and thicker at the other; some had two or three points, being double or triple hairs; some were two inches long, others not more than half an inch; a few were fine and silky, but the majority were more like the hair of the pubes or whiskers than those of an infant.

Chemical Examination.—A certain quantity of the fat was heated in a water-bath at 212° F., so as to expel all moisture. It was then accurately weighed.

a. The melted mass was then boiled repeatedly in pure anhydrous æther until everything soluble in that menstruum was extracted. For insoluble residue *vide* (*e.*). The mixed æthereal solutions were allowed to cool, and then thrown on a filter of white bibulous paper, and the residue repeatedly washed with cold æther. This residue was then carefully removed from the filter, from which any adhering particles were also removed by means of boiling æther; it, together with the washings, were then exposed to the heat of a water-bath to expel the æther. A transparent oily-looking substance remained, which on cooling solidified into a mass not unlike tallow in appearance and consistence. This was a fat, therefore, *soluble in boiling æther, but insoluble in cold.*

b. The cold æthereal solution, separated by the filter (*a.*), was also evaporated to dryness in a water-bath, and the weight of the residue was accurately taken.

An oily, transparent, and slightly-yellowish body remained behind, very similar in appearance to olive-oil, which upon cooling became converted into a semi-fluid mass, slightly opalescent.

c. The residues from the æthereal solutions (*a.*) and (*b.*) were both treated with boiling alcohol, spec. grav. 0·813. They dissolved

* Communicated by the Author.

with facility, furnishing solutions which upon cooling became opalescent and muddy, and by repose deposited white pearly flocculi. These occurred to the greatest extent in the solution of the body insoluble in cold æther; in fact they formed two-thirds of its weight. These flocculi having been separated by filtration, and the filters well washed with cold alcohol, the solutions were evaporated to dryness in a water-bath, when a transparent, yellowish, oily body remained behind, which upon examination was found to possess all the characters of elaine.

d. The light flocculent substance, when separated from the filter, was acted upon by an excess of a warm concentrated solution of caustic potash. The resulting soap was then repeatedly treated with warm alcohol, spec. grav. 0·835, in which it almost entirely dissolved, proving the absence of stearic acid. The alcoholic solution was then evaporated nearly to dryness, and the residue treated with tartaric acid in excess. The solution having been filtered (to separate the bitartrate of potash, &c. formed), the excess of tartaric acid present was then removed by the addition of an excess of carbonate of lime in fine powder, and the solution again filtered and evaporated to a syrup, when a body remained possessing a sweet and pleasant taste, and having all the characters of glycerine.

The precipitated bitartrate of potash, &c., when boiled with absolute alcohol, yielded a solution which contained a large proportion of margaric acid.

e. The substances insoluble in boiling æther (*a.*) were then repeatedly treated with boiling alcohol, which removed small quantities of chloride of sodium and a peculiar extractive matter; this substance precipitated infusion of galls, but was not gelatine; it closely resembled the body called osmazome in its properties, but its exact nature could not be determined on account of the small quantity present.

f. The insoluble residue from (*e.*) was then examined under a microscope; it appeared to consist of little more than epidermoid or pavement-epithelium cells, with a few hairs; these cells were lighter than water; they were dissolved in warm nitric acid, giving an orange-coloured solution, which assumed a still deeper colour upon the addition of ammonia. When boiled in a solution of potash, they became gelatinous and disintegrated; when ignited, they gave a white ash (*g*).

The hairs did not differ from those previously described, a few of which had escaped separation by the process adopted.

g. Upon igniting the fatty matter in an open platina capsule, it burnt off with a bright smoky flame, and left a carbonaceous residue, which upon continued ignition became a white ash; this consisted chiefly of carbonate and phosphate of lime, with a little phosphate of iron, and a small per-centage of chloride of sodium and carbonate, sulphate and phosphate of soda (0·834 per cent.).

A quantitative analysis of the fatty matter gave the following results:—

Quantitative analysis (after separation of hair):—

Elaine soluble in hot æther	4·69	84·69
Elaine soluble in cold æther	80·00	
Margarine (margarate of glycerine)		11·68
Extractive matter and chloride of sodium		1·24
Epidermoid cells with hair		2·39
		100·00

The inorganic constituents consisted of—

Soluble salts	Carbonate of soda		traces
	Phosphate of soda		
	Sulphate of soda		0·209
	Chloride of sodium		
Insoluble salts	Carbonate of lime	0·243	
	Carbonate of magnesia	trace	
	Phosphate of lime (tribasic)	0·243	
	Phosphate of magnesia	trace	
	Phosphate of iron	some	
	Sulphate of lime	minute trace	
	Silica and charcoal	0·139	
	Per cent.	0·834	

Reasoning upon the above analysis, &c., the author concludes that it was not an ovarian fœtation; that it was not the result of a fœtus remaining in the ovary, and subsequently entering into putrefaction and decomposition; because, *first*, no bones were discovered in the contents of the cyst; *secondly*, there was not enough carbonate and phosphate of lime, even had these disintegrated; *thirdly*, the hairs were decidedly not fœtal, but adult; and *lastly*, the earthy salts were distinctly traced to the epidermoid or epithelial cells.—*Edinb. Medico-Chirur. Quart. Journ.*, Dec. 1848, p. 111.

On a Series of Organic Alkalies homologous with Ammonia. *By* A. Wurtz.

The history of the ammoniacal compounds, so complete and so important in a theoretical point of view, forms in some measure a transition between inorganic and organic chemistry. Ammonia should decidedly be regarded as the most simple and the most powerful of the organic bases; and it would be for all chemists the type of that numerous class of bodies, did it not differ in one undoubtedly important character, but to which an exaggerated value has been attributed. Ammonia contains no carbon. This difference however of composition does not suffice, in my opinion, to separate ammonia from the organic bases; I have succeeded, in fact, in converting this alkali into a true organic compound, by adding to it the elements of the hydrocarbon C^2H^2 or C^4H^4, without depriving it of its characters of a powerful base, or of its most striking properties, for instance its odour. By adding to the elements of ammonia, NH^3, the elements of 1 equiv. of methylene, C^2H^2, the compound C^2H^5N,

which may be called methylic ammonia, is obtained. By adding to ammonia the elements of ethylene, C^4H^4, ethylic ammonia, C^4H^7N, is obtained.

The compounds C^2H^5N and C^4H^7N may be viewed as methylic æther, C^2H^3O, and ordinary æther, C^4H^5O, in which the equivalent of oxygen is replaced by 1 equiv. of amidogen, NH^2; or as ammonia in which 1 equiv. hydrogen is replaced by methylium, C^2H^3, or ethylium, C^4H^5. The following formulæ will exhibit the relations which exist between these substances and ammonia:—

H^3N, ammonia.	NH^2, H, *hydramide.*
C^2H^5N, methylic ammonia.	NH^2, C^2H^3, *methylamide.*
C^4H^7N, ethylic ammonia.	NH^2, C^4H^5, *ethylamide.*

I shall employ in preference the names methylamide and ethylamide to designate these new bases.

In the present communication I shall restrict myself merely to communicating the circumstances under which these substances are produced, and to communicating the results of some analyses which establish their composition. They are produced under three different circumstances,—1st, by the action of potash on *cyanic æthers*; 2nd, by the action of potash upon *cyanuric æthers*; and 3rd, by the action of potash upon the *ureas*. These reactions will be best exhibited by a few formulæ:—

$$\underset{\text{Cyanic acid.}}{C^2NO, HO} + 2KO + 2HO = 2CO^2, KO + \underset{\text{Ammonia.}}{H^3N}$$

$$\underset{\text{Cyanate of methylene.}}{C^2NO, C^2H^3O} + 2KO + 2HO = 2CO^2, KO + \underset{\text{Methylamide.}}{C^2H^5N}$$

$$\underset{\text{Cyanic æther.}}{C^2NO, C^4H^5O} + 2KO + 2HO = 2CO^2, KO + \underset{\text{Ethylamide.}}{C^4H^7N}$$

Cyanuric acid and the cyanuric æthers being isomeric with the cyanic compounds, it will suffice to multiply the preceding formulæ by 3 to explain the second mode of formation. With respect to the ureas, the following equations will show how they give rise to these bases:—

$$\underset{\text{Urea.}}{C^2H^4N^2O^2} + 2KO + 2HO = 2CO^2, KO + H^3N + H^3N$$

$$\underset{\text{Acetic urea.}}{C^4H^6N^2O^2} + 2KO + 2HO = 2CO^2, KO + H^3N + C^2H^5N$$

$$\underset{\text{Metacetic urea.}}{C^6H^8N^2O^2} + 2KO + 2HO = 2CO^2, KO + H^3N + C^4H^7N$$

Hydrochlorate of Methylamide.—I obtained this salt by boiling cyanurate of methylene with an excess of potash in an apparatus arranged so that the vapours of methylamide, after having passed through a refrigerator, were condensed in a receiver containing a little pure water. The excessively caustic liquid thus obtained has a strong odour of ammonia, but does not contain a trace of that alkali; for if saturated with hydrochloric acid and evaporated to dryness, the residue, consisting of hydrochlorate of methylamide, dissolves very readily in hot absolute alcohol. The salt crystallizes

on cooling in beautiful laminæ, which are iridescent so long as they float in the liquid, and assume a nacreous appearance when dry. Analysis gave—

Carbon	17·4	2 =	12	17·7
Hydrogen	8·7	6	6	8·8
Chlorine	52·2	1	35·5	52·5
Nitrogen	21·7	1	14	21·0

Hydrochlorate of Methylamide and Chloride of Platinum.—Beautiful golden scales, which are soluble in hot water, and contain $ClH, C^2 H^5 N PtCl^2$. Analysis gave—

Carbon	5·3	2 =	12	5·0
Hydrogen	2·8	6	6	2·5
Chlorine	44·4	3	106·5	44·9
Platinum	41·4	1	98·6	41·5
Nitrogen	..	1	14	

Nitrate of Methylamide—beautiful transparent prisms, which are soluble in alcohol.

Hydrochlorate of Ethylamide.—I have prepared this substance both with cyanic and with cyanuric æther. It dissolves readily in absolute alcohol, and crystallizes in laminæ; it melts below 212°, and solidifies on cooling into a crystalline mass. When distilled with burnt lime, it gives off ethylamide in the form of an excessively caustic liquid, which diffuses a strong odour of ammonia. This liquid precipitates all the metallic salts, and even the salts of magnesia. In solutions of salts of copper it at first forms a blue precipitate, which it afterwards redissolves, forming an azure-blue liquid; it produces a green precipitate in salts of nickel, which however is not redissolved, as is the case with ammonia. I ascertained that the liquid did not contain a trace of ammonia, by saturating it with hydrochloric acid; the residue, evaporated to dryness, dissolved entirely in absolute alcohol, and formed with chloride of platinum a double salt, the analysis of which will be found below.

The composition of the hydrochlorate of ethylamide is represented by the formula $ClH, C^4 H^7 N$. Analysis gave—

Carbon	28·9	29·4	4 =	24	29·4
Hydrogen	9·9	9·9	8	8	9·8
Chlorine	43·7	..	1	35·5	43·6
Nitrogen	17·5	..	1	14	17·2

Hydrochlorate of Ethylamide and Chloride of Platinum—golden scales, soluble in water. They gave on analysis—

Carbon	9·5	4 =	24	9·5
Hydrogen	3·2	8	8	3·2
Chlorine	42·0	3	106·5	42·4
Nitrogen	..	1	14	
Platinum	39·0	1	98·6	39·2

I hope soon to give a complete history of these alkalies.—*Comptes Rendus*, Feb. 12.

On Ricinoleic Acid. *By* L. Svanberg *and* G. Kolmodin.

Castor oil was saponified with caustic potash and the soap decomposed with muriatic acid; the fatty acids were entirely freed from chloride of potassium and glycerine by washing with water, and were then exposed to a temperature of 32° to 20°, when the ricinostearic acid and the other acids separated, and could be removed by filtration at this low temperature. What passed through the filter was mixed with caustic ammonia, but not in sufficient quantity to dissolve the whole of the fatty acid. The ammonia soap was precipitated with chloride of barium, and the baryta salt purified by recrystallization from its solution in alcohol as long as the crystals exhibited any difference in the amount of baryta.

In the analysis of the baryta salt, which had been previously dried *in vacuo* over sulphuric acid and had been crystallized five times from an alcoholic solution, we obtained 20·80 per cent. baryta. As the salt might possibly have been an acid one, it was digested for several hours with hydrate of baryta, after which it was again several times recrystallized from alcohol. A salt which had been recrystallized nine times furnished 20·78 baryta, and the atomic weight according to this is 3639·18.

The ricinoleate of baryta gave on analysis—

Carbon	58·776	36	59·157
Hydrogen	8·964	33	9·099
Oxygen	11·480	5	10·937
Baryta.....	20·780	1	20·897

which agrees with the formula $BaO + C^{36} H^{33} O^5$. The composition of the anhydrous acid is, according to analysis and calculation—

	Found.	Calculated.
Carbon	74·193	74·784
Hydrogen	11·418	11·389
Oxygen	14·389	13·827

The atomic weight of the anhydrous ricinoleic acid, found by calculation, is 3616·2, which differs somewhat from the directly-determined number, but not more than is frequently the case in compounds which possess a high atomic weight. The ready solubility of the ricinoleate of baryta in hot, and the sparing solubility in cold alcohol, especially favours the separation of this acid from those simultaneously formed in the saponification of the castor oil, as only one-third per cent. of this salt dissolves in cold alcohol of 0·815 spec. grav., and it crystallizes from the hot alcoholic solution on cooling in laminar crystals. When the baryta salt of an impure acid (altered by exposure to the air) is treated with alcohol, a large quantity remains dissolved in the cold alcohol. Both the free acid, as well as its salts, dissolved in alcohol, experience a change by exposure to the atmosphere, other acids being produced. This behaviour is peculiar to most of the fatty acids when exposed for any length of time to the influence of oxygen, especially in the fluid state.

The salts of lime and lead are also very readily soluble in hot alcohol; but their solubility at different temperatures does not vary very much, especially the lime salt, so that this is not so well adapted as the baryta salt for studying the acid.

The affinity of this acid with Gottlieb's pure oleic acid is worthy of attention; it is such that these two acids might be regarded as differing solely in the number of the atoms of oxygen, the hydrocarbon radical being the same.

Pure ricinoleic acid, separated from its baryta salt by muriatic acid, is a very weak acid, the alcoholic solution of which faintly reddens blue litmus-paper. It solidifies at about 32°.—*Journ. für Prakt. Chem.*, xlv. p. 431.

Bread for Diabetic Patients. Communicated by Dr. PERCY, F.R.S.

It appears to be now generally admitted, that in the treatment of Diabetes Mellitus, amylaceous matter should in a greater or less degree be excluded from the diet. But, as is well known, under such restriction of food the diabetic patient soon becomes weary of the ordinary kinds of azotized matter, as beef, mutton, &c. Hence various substitutes for common bread have been proposed. Some years ago my friend Mr. Morson, of Southampton Row, London, prepared, at my request, specimens of bread containing gluten in various proportions. However, the result was not satisfactory*; it was only relished by the patient when it contained a considerable quantity of starch; and when the proportion of gluten was increased beyond a certain amount, it became so tough and tenacious as to be very difficult of mastication. I have also made trial of gluten bread, brought from Paris by Mr. Morson, but with no better success. Recently Dr. Prout has published a receipt for a kind of bread devised by his patient the late Rev. J. Rigg (*vide* Stomach and Renal Diseases, 5th ed. p. 44); and this is probably the best substitute for common bread which has hitherto been proposed. Some time ago Mr. Charles F. Palmer of this town prepared for me with great care, specimens of bread from Dr. Prout's receipt; but patients to whom it was given complained of the difficulty in swallowing it, owing to the large quantity of bran which it contained. Mr. Palmer then suggested the matter of rasped potatoes, left after the complete removal of the starch by washing, to replace the bran. He carried the suggestion into practice, and produced a kind of bread which I think well deserves the attention of the profession. It has been extensively employed in the General Hospital of this town, especially by my friends Dr. James Johnstone and Dr. Fletcher, and also by several private practitioners, with decided advantage. In composition it may be considered as Mr. Rigg's bread, in which the bran has been replaced by the residual matter of the potato above-mentioned. And in the fact of its being rendered light and porous by hydrochloric acid and carbonate of soda, precisely as in the prepara-

* I do not mean by this to assert, that bread deprived of a portion of its starch is not preferable to common bread for diabetic patients.

tion of Dodson's unfermented bread, it is, as must be obvious, an expensive article; but with many diabetic patients this will not be an object of consideration. It is improved in taste by being slightly toasted and eaten warm. I here subjoin Mr. Palmer's receipt:—

Take the ligneous matter of 16 lbs. of potatoes washed free from starch, ¾ of a pound of mutton suet, ½ a pound of fresh butter, 12 eggs, ½ an ounce of carbonate of soda, and 2 oz. of dilute hydrochloric acid. This quantity to be divided into eight cakes, and in a quick oven baked until nicely browned. At first gum-arabic in sensible quantity was also introduced into this bread, on the ground of the assertion of Professor Graham, that when that substance is taken by the diabetic patient, the proportion of sugar evolved from his system is not thereby increased, and that consequently it might probably supply matter for pulmonary oxidation. However, it was found that it rendered the bread tenacious and disagreeable; so that its use was subsequently abandoned. I wish it to be understood that whatever merit there may be in the production of this bread, it is entirely due to Mr. C. F. Palmer. My friend Dr. Evans suggests, and I think with reason, that this bread would probably be improved by the addition of a certain proportion of bran. Some gluten might also be added with advantage.

Birmingham, March, 1849.

CHEMICAL PREPARATIONS.

Comparative Examination of the different Methods of preparing the Iodide of Lead. By T. Huraut.

Several methods of preparing the iodide of lead have been described, each of which furnishes tolerably satisfactory results. When executed with care, they yield a pure product, and the quantity obtained is not far below what theory requires. It is consequently indifferent which of these processes is employed when only small quantities of iodide are prepared; but when these are considerable, the differences become sufficiently great not to be neglected. There is another not less important condition, which ought constantly to be kept in view with every preparation; it is the obtaining a beautiful product. Now it has long since been observed, that the mode of operating and the nature of the substances employed in the preparation of the iodide of lead, have a very considerable influence on the appearance of the iodide.

Before describing my experiments, I must observe that each process has been repeated twice, and each operation performed under the same conditions, in order to obtain accurate results comparable with one another; I may add, that in all cases distilled water was employed; that the purity of the iodine and of the iodide of potassium was previously ascertained; that the nitrate and neutral acetate of lead were prepared expressly for these experiments; and lastly, that in each experiment a weight of iodine or of iodide was em-

ployed which should furnish according to theory 18·20 grms. iodide of lead.

1. *Process by Iodide of Potassium.*—This process is the oldest employed; it consists in decomposing the iodide of potassium with a salt of lead. The French Codex prescribes the neutral acetate; but that salt has been generally abandoned, since Messrs. Depaire and Boudet have shown that the iodide of lead dissolves in considerable quantity in the acetate of potash which is formed by the double decomposition of the iodide of potassium and acetate of lead. The loss, according to M. Boudet, is about one-tenth.

13·10 grms. of iodide of potassium, containing 10 grms. of iodine, were treated with neutral acetate of lead, the weight of the precipitated iodide was 15·70 to 15·80 grms. To avoid the loss to which the use of acetate of lead gives rise, M. Boudet proposed to substitute for this salt the nitrate of the same base. On treating 13·10 grms. of pure iodide of potassium with a solution of nitrate of lead, 17·50 to 17·55 grms. of iodide were obtained.

According to M. Thévenot, this loss may be avoided by pouring into the liquid above the iodide of lead a little nitric acid, which precipitates the greater portion of the iodide of lead held in solution. I tried this plan, and obtained with the same proportions 17·30 grms. iodide of lead. On the other hand, I treated the wash-waters from the first experiment with a sufficient quantity of nitric acid to decompose the acetate of potash they contained, and I collected 1·45 grm. of iodide of lead in brilliant scales.

The iodide of lead prepared with iodide of potassium is of a beautiful lemon-yellow colour, and entirely soluble in boiling water. Sometimes it is obtained in the form of minute brilliant laminæ, at other times without any crystalline form. This effect, which occurs in all the methods of preparing the iodide of lead, appears to me to be attributable to the more or less concentrated state of the liquors.

2. *Process by Iodide of Sodium.*—Hitherto the iodide of sodium has never been employed, as far as I am aware, owing to its liability to change by exposure to the air and heat. However, as it may be obtained in a pure state in the liquid form, I was curious to know the results it would yield, and converted 10 grms. of iodine into iodide of sodium, which furnished with acetate of lead 15·90 to 16·10 of iodide, and with the nitrate 16·85 to 16·95. This iodide is perfectly similar to that obtained with the iodide of potassium, and is of a lemon-colour.

3. *Process by Iodide of Calcium.*—All the soluble iodides may be used for the preparation of iodide of lead, but not with the same advantage. Thus those, the preparation of which is attended with much difficulty or requires long time, are not used, whilst those which are readily and quickly prepared are employed indifferently. Till of late the iodide of calcium has not received any application; but a few months ago M. Criquellon having described a very simple and cheap method of obtaining it, this iodide may now be turned to account. To see whether it offered any advantage in the prepa-

ration of the iodide of lead, I decomposed a solution containing 10 grms. of iodine by a solution of nitrate of lead, and obtained 17·70 to 17·60 grms. of a beautiful orange-yellow iodide of lead. The second experiment, made so as to give a crystalline iodide, furnished a product of remarkable brilliancy.

I then treated a similar solution of iodide of calcium with acetate of lead; the weight of the precipitate was 17·25 to 17·40. This iodide was likewise of a beautiful orange-yellow colour.

4. *Process by Iodide of Iron.*—In a memoir presented to the Ecole de Pharmacie of Paris in 1840, M. Girault showed that the iodide of iron might be employed with advantage for the preparation of the iodide of lead; he pointed out the inconveniences which attend the use of this compound, and made known the precautions which should be taken to avoid them. Subsequently, in 1847, M. Gaffard, without being acquainted with the researches of M. Girault, likewise proposed the iodide of iron for the preparation of the iodide of lead; the prescription, however, which he has given has been justly criticised by M. Thévenot. But even in the corrected formula the latter chemist has retained too large a proportion of iron. Although an excess of iron is rather useful than otherwise, nevertheless I see no reason for employing three times more of that metal than is required.

10 grms. of iodine, converted into iodide of iron, and treated with neutral acetate of lead, afforded 16·70 to 16·75 iodide of lead. I obtained a more satisfactory result by precipitating the iodide of iron from 10 grms. of iodine with a solution of nitrate of lead; the product weighed 17·50—17·50 grms. The iodide of lead obtained from the iodide of iron is of an orange-colour, and dissolves entirely in boiling water. It possesses the same characters whether the acetate or the nitrate of lead has been employed.

5. *Process by Iodide of Zinc.*—I am not aware that the iodide of zinc has been proposed for the preparation of the iodide of lead, and nevertheless this salt is the one now most frequently employed; its great solubility and the readiness with which it is obtained will readily account for the preference given to it; it is moreover not altered in the air. 10 grms. of iodine, converted into iodide of zinc, furnished 17·05 to 17·15 grms. iodide of lead on precipitation with the neutral acetate, and 17·40 to 17·45 with nitrate of lead; the iodide is of a pale orange-yellow colour, sometimes lemon-coloured.

6. *Process by the Double Iodide of Potassium and Lead.*—In a recent paper on the iodide of lead, M. Thévenot has proposed a new process for preparing this salt; it is founded on the decomposing action of water upon the combination which the iodide of potassium forms with the iodide of lead. This compound is prepared in the following manner. Take—

Iodine	10 parts
Iodide of potassium	10 ...
Distilled water	5 ...
Divided lead	a large excess
Nitrate of lead	10 parts

The four first substances are mixed in a beaker, and set aside for twenty-four hours. The whole of the iodine has then disappeared, and only the excess of lead is left; this is coated with a yellowish-white substance of a crystalline appearance, which is the potassio-iodide of lead. To obtain the iodide of lead which this compound contains, it suffices to agitate it with water, which decomposes it into iodide of potassium and iodide of lead. The dissolved nitrate of lead is then poured into the liquid, which decomposes the whole of the alkaline iodide.

The above quantities should give according to theory 32·07 grms. iodide of lead; they furnished 31·40—31·45. This iodide is slightly shining, and of a pale lemon colour. When seen alone, it appears satisfactory; but when compared with the iodides obtained by the previous processes, a difference is perceptible, which is far from being to its advantage.

Having found by experiment that the iodide of lead prepared with the iodide of potassium was of a beautiful lemon colour, I was led to imagine, from the result obtained by M. Thévenot's process, that since about three-sevenths of the product derived from the decomposition of the iodide of potassium were of a fine quality, the four-sevenths furnished by the decomposition of the double salt by water must be of a far less lively colour. Experiment confirmed this supposition; in fact the iodide so obtained is of so pale a yellow tint that one might be led to think it consisted in greater part of oxy-iodide. Moreover, its fatty appearance is not at all pleasant to the sight. I have repeated this experiment several times, and always with the same results. In these experiments the weight of the iodide produced from the decomposition of the potassio-iodide of lead by water alone was on the average 17·80; theory requires 18·20 grms.

From these results I conclude, that, in the preparation of the iodide of lead, the nitrate of lead, on account of the greater product, is more œconomical, notwithstanding its high price, than the acetate, and should always be preferred to it whatever process is employed.

That the process by iodide of calcium is most advantageous as regards the quantity and quality of the product.

That since the two processes by iodide of iron and by iodide of zinc yield an equally beautiful product and in nearly the same amount, it is indifferent which is used.

That the process by iodide of sodium has no advantage; that by iodide of potassium is less œconomical, as this salt costs as much as the iodine, with which the other iodides may be readily prepared without loss and at little expense, and furnishes nearly one-fourth less for the same weight. In fact, when iodide of potassium and acetate of lead are employed, there is a loss of 10 per cent.; but the greater portion of this loss may be avoided by substituting the nitrate for the acetate of lead, or by pouring into the supernatant liquid a sufficient quantity of nitric acid to decompose the acetate of potash.

Lastly, that the process by the double iodide of potassium and lead, although yielding a larger product than all the others, is less

advantageous, in the first place from its requiring iodide of potassium, and secondly from the inferior quality of the iodide which it furnishes.—*Journ. de Pharm.*, Jan. 1849.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On Vitrifiable Pigments. By A. Wæchter.

[Continued from p. 108.]

Black and Gray Colours for painting upon Porcelain.

Iridium Black.

Iridium, as obtained in commerce from Russia in the state of a fine gray powder, is mixed with an equal weight of calcined chloride of sodium, and heated to a faint red in a porcelain tube through which a current of chlorine is passed. In this manner a portion of the iridium is converted into the bichloride of iridium and sodium, which is dissolved out with water from the ignited mass. The aqueous solution of the double salt is evaporated to dryness with carbonate of soda, and then extracted with water, which furnishes black sesquioxide of iridium. This is dried and mixed with twice its weight of lead glass (prepared by fusing together 12 parts of minium, 3 parts of white sand and 1 part of calcined borax), and ground upon a plate of glass. The iridium, which remained undecomposed in the first treatment with sea-salt and chlorine, is again submitted to the same treatment.

Iridium Gray.

1 part of the sesquioxide of iridium, 4 parts of oxide of zinc and 22 parts of lead glass (prepared by fusing together 5 parts of minium, 2 parts of sand and 1 part calcined borax) are intimately mixed and ground fine upon a plate of glass. On microscopical examination of the iridium pigments after they have been burnt-in upon porcelain, the sesquioxide of iridium is seen to be suspended in the transparent fused lead glass. It is owing to the unalterability of the sesquioxide of iridium that it admits of being mixed with all other vitrifiable colours without injuriously affecting the tints, as is the case with all the other vitrifiable gray and black pigments.

Black from Cobalt and Manganese.

2 parts of sulphate of cobalt deprived of its water of crystallization, 2 parts of dry protosulphate of manganese and 5 parts of nitre are intimately mixed, and heated to redness in a Hessian crucible until the whole of the nitre is decomposed. The calcined mass, exhausted with boiling water, furnishes a deep black powder, which consists of a combination of oxide of cobalt and oxide of manganese. 1 part of this compound is mixed with $2\frac{1}{2}$ parts of lead glass (pre-

pared by fusing together 5 parts of minium, 2 parts of sand and 1 part calcined borax), and ground fine upon a plate of glass.

Gray from Cobalt and Manganese.

2 parts of the above compound of the oxide of cobalt and manganese, 1 part oxide of zinc and 9 parts of lead glass (prepared by fusing together 5 parts of minium, 2 parts of sand and 1 part of calcined borax) are mixed and ground fine.

These black and gray pigments are far less expensive to prepare than those from iridium, and are not inferior to them in colour; but they do not mix so well with other colours, and when baked several times they vary their tint somewhat, which renders their application less certain. When these colours burnt-in upon porcelain are examined under the microscope, it is seen that the oxide of cobalt and manganese is not dissolved by the lead glass, but merely suspended in it.

Besides these colours a very infusible black is used in painting, which is not acted upon by the superposed colours in the fusion; it is the

Ground Black,

which consists of 5 parts of blue violet (gold-purple), $1\frac{2}{3}$ part of oxide of manganese and cobalt and $1\frac{2}{3}$ part of oxide of zinc; these are intimately mixed and ground fine upon a plate of glass.

White for covering.

1 part minium, 1 part white sand and 1 part crystallized boracic acid are well mixed, and fused in a porcelain crucible. This white enamel has the peculiarity of forming a colourless clear glass when quickly cooled, for instance when poured into water, while when slowly cooled it remains perfectly white and opake. On heating the clear glass to its melting-point, it loses its transparency, and becomes opake as before. This property it possesses in common with the enamels, the opacity of which is produced by arsenic or tungstic acid; probably the opacity in the present case is produced by the separation of silicate of lead, as in the white enamels by arseniate or tungstate of potash or by oxide of zinc. It is however of excessive minuteness; for under the microscope, even with the highest power, the glass merely exhibits a yellowish turbidness, and no individual particles are visible.

This white serves for marking the lightest part of the pictures, where it is impossible to produce them by exposing the bare surface of the white porcelain; it is also frequently mixed in small quantity with the yellow and green pigments, to make them cover well.

Lead Flux.

A colourless lead glass for touching up those parts of the painting which have remained dull, and for mixing with those pigments which are not easy of fusion, is obtained by mixing together 5 parts of minium, 2 parts of white sand and 1 part of calcined borax.

Red and Brown Vitrifiable Pigments derived from Peroxide of Iron for painting upon Porcelain.

Yellow-Red.

Anhydrous sulphate of the peroxide of iron is heated to redness on a dish in an open muffle, and constantly stirred with an iron spatula until the greater portion of the sulphuric acid has been expelled, and a sample mixed with water upon a glass plate exhibits a beautiful yellowish-red colour; after cooling, the peroxide of iron is freed by washing with water from any undecomposed sulphate and dried. To prepare the pigment, 7 parts of the yellowish-red peroxide of iron are well mixed with 24 parts of lead glass (prepared by fusing together 12 parts of minium, 3 parts of sand and 1 part of calcined borax), and ground fine upon a plate of glass.

Brown-Red.

When the persulphate of iron is heated to redness until the whole of the sulphuric acid is expelled and a sample exhibits a dark red colour, the peroxide of iron is well suited for a brownish-red pigment, which is prepared in the same manner as directed for the yellowish-red.

Brown-Red (Pompadour).

When the persulphate is heated still more strongly, it is deprived of its loose consistence, becomes heavier, and acquires a bluish-red colour. To hit this point exactly when the oxide of iron has assumed the desired carmine tint is not so easy, as it changes very rapidly at these temperatures.

The pigment is prepared by mixing 2 parts of the purple-coloured peroxide of iron with 5 parts of lead glass, obtained by fusing together 5 parts of minium, 2 parts of sand and 1 of calcined borax.

Chestnut-Brown.

This colour, of various shades even to black, is acquired by the peroxide of iron at still higher degrees of heat than required for the preparation of red colours; the pigments are prepared by mixing 2 parts of the chestnut-brown peroxide of iron with 5 parts of lead glass, prepared by fusing together 12 parts of minium, 3 parts of sand and 1 part of calcined borax.

Chamois.

1 part of the hydrate of the peroxide of iron, prepared by precipitating the peroxide of iron with ammonia, is mixed with 4 parts of the lead glass described in the preceding, and the mixture ground fine on a plate of glass. This colour is laid on very thin, and serves to produce a yellowish-brown ground.

Flesh Colour.

1 part red peroxide of iron, 4 parts of dark yellow II. and 10 parts of lead glass, prepared as described under chestnut-brown, are well mixed and ground fine upon a plate of glass. This colour can

also only be employed in a thin layer. Various tints may be given to it by mixing it with red peroxide of iron, sky-blue or dark yellow II. The red of the cheeks and lips are painted upon it with Pompadour red.

When the above colours are burnt-in upon porcelain, it is distinctly seen under the microscope that the peroxide of iron is suspended unaltered in the clear lead glass; at least the quantity dissolved by the fused lead glass is so small that it is not perceptibly coloured.

Various Brown Pigments for painting upon Porcelain.

Light Brown, I.

6 parts of dry protosulphate of iron, 4 parts of dry sulphate of zinc and 13 parts of nitre are well mixed, and heated to redness in a Hessian crucible until the whole of the nitre is decomposed. When cold, the crucible is broken, the residue removed, and separated by boiling with water from soluble matters. A yellowish-brown powder remains, which is a combination of oxide of zinc with peroxide of iron. The pigment is made by mixing 2 parts of this compound with 5 parts of lead glass, prepared by fusing together 12 parts of minium, 3 parts of sand and 1 part of calcined borax.

Light Brown, II.

2 parts of dry sulphate of iron, 2 parts of dry sulphate of zinc and 5 parts of nitre are treated in the same manner as described for light brown I. The resulting compound of oxide of zinc and iron is of a lighter tint; the pigment is prepared from it as above.

Light Brown, III.

1 part of dry sulphate of iron, 2 parts of dry sulphate of zinc and 4 parts of nitre are treated as directed for I. and II.

The light brown colours, after having been burnt-in upon porcelain, exhibit under the microscope the transparent particles of the yellowish oxide of iron and zinc suspended in the colourless lead glass.

Bister-Brown, I.

1 part dry sulphate of manganese, 8 parts dry sulphate of zinc, 12 parts dry sulphate of iron and 26 parts nitre are treated as directed for light brown I., and the resulting dark brown powder (a combination of the oxides of zinc, iron and manganese) mixed with $2\frac{1}{2}$ times its weight of lead glass of the same composition as for light brown I.

Bister-Brown, II.

1 part dry sulphate of manganese, 4 parts dry sulphate of iron, 4 parts dry sulphate of zinc and 12 parts nitre are treated as for bister-brown I. The colour is somewhat darker.

Sepia-Brown, I.

1 part dry sulphate of iron, 1 part dry sulphate of manganese, 2 parts dry sulphate of zinc and 5 parts nitre are treated as directed

for light brown I., and the grayish-brown pigment thus obtained mixed with $2\frac{1}{2}$ times its weight of lead glass of the above composition.

Sepia-Brown, II.

1 part calcined sulphate of iron, 2 parts calcined sulphate of manganese, 6 parts calcined sulphate of zinc and 10 parts nitre are treated as for sepia-brown I.

Dark Brown.

1 part dry sulphate of cobalt, 4 parts dry sulphate of zinc, 4 parts dry sulphate of iron and 10 parts of nitre are mixed and treated as directed for light brown I. The resulting beautiful dark reddish-brown combination of the oxides of cobalt, zinc and iron is mixed with $2\frac{1}{2}$ times its weight of the same lead glass as for the preceding colours.

Chrome-Brown.

1 part of hydrated peroxide of iron is intimately mixed with 2 parts of the chromate of the protoxide of mercury, and then heated to redness in a dish in an open muffle to expel the whole of the mercury. The dark reddish-brown compound of the oxides of chromium and iron is mixed with 3 times its weight of lead glass, prepared by fusing together 5 parts of minium, 2 parts of sand and 1 part of calcined borax.

When examined under the microscope, after being burnt-in upon porcelain, these different brown colours also show that the dark compounds are merely suspended in the lead glass, and not, or merely to a small extent, dissolved. The direction above given for preparing the coloured combinations of the oxides in the dry way for the bodies which constitute the different brown pigments, is cheaper and more certain than the precipitation of the mixed solutions by carbonate of soda and calcination of the washed precipitate, which also answers. If however the several oxides were to be mixed with the lead glass separately instead of combined, the colours would not be pure, that is to say, they would exhibit after the firing different tints in a thick and a thin layer; they would moreover possess a totally different colour before the burning from that which they acquire after that operation, and would thus contribute to deceive the artist.—Liebig's *Annalen*, Jan. 1849.

Method of removing Ink Stains from Linen made with so-called Indelible Ink. By M. Sourisseau.

The linen is dipped in chlorine water until the silver is converted into chloride, which is recognised by the white colour the stains have assumed; it is then rinsed in soft water, and afterwards washed in water to which some ammonia has been added, which quickly dissolves the chloride of silver, leaving no trace of the ink.—*Journ. der Pharm.*, Feb. 1849.

THE CHEMICAL GAZETTE.

No. CLV.—April 2, 1849.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Observations on Anhydrous Nitric Acid. By M. Deville.

By treating nitrate of silver with absolutely dry chlorine, M. Deville has succeeded in isolating anhydrous nitric acid, the existence of which is proved by numerous analyses.

This beautiful substance forms perfectly transparent colourless crystals of great brilliancy, and capable of attaining a considerable size when slowly deposited in a current of gas strongly cooled. They are prisms of six faces, and are apparently derived from a right rhombic prism. They melt at a temperature a little above 85° F., and boil at about 113°. At 50° the tension of this substance is very considerable. In contact with water it evolves much heat, and dissolves without any disengagement of gas or the production of any colour, and then furnishes with baryta nitrate of baryta. Under the influence of heat its decomposition appears to begin very near its boiling-point, which prevents the density of its vapour being determined by M. Dumas' process.

The method by which M. Deville procured the anhydrous acid is very simple; but the ease with which it penetrates caoutchouc tubes necessitates the uniting of all the parts of the apparatus before the blowpipe. The author employs a U-shaped tube, capable of containing 500 grms. of nitrate of silver dried in the apparatus at 356° in a current of dry carbonic acid. To this tube is joined another U-shaped tube of considerable size, and furnished at the bottom with a small spherical reservoir, in which a liquid, which is constantly developed during the operation, and which is excessively volatile (nitrous acid?), collects. The tube containing the nitrate of silver is immersed in water covered with a thin layer of oil, and heated by means of a spirit-lamp communicating with a reservoir at a constant level. The chlorine is evolved from a glass gasometer, and its displacement is produced by a slow and constant flow of concentrated sulphuric acid; the chlorine is passed over chloride of lime, and then over pumice-stone moistened with sulphuric acid. At the ordinary temperature nothing appears to be produced; the nitrate of silver must be heated to 203°, and the temperature then immediately lowered to 136° or 154°, beyond which it should not go. At first some hyponitric acid is developed, recognizable from its colour and its ready condensation; then, as soon as the tempera-

ture has reached the lowest point, the production of crystals commences, and they soon obstruct the recipient cooled to —6° F. They are always deposited on the portion of the receiver which is not immersed in the freezing mixture: and M. Deville has found that ice alone sufficed to determine their production. The gases are coloured, and the spherical reservoir of the cooled tube contains a small quantity of liquid, which must be removed from the apparatus before transferring the nitric acid into another vessel. This last operation is easily effected by substituting a current of carbonic acid for the one of chlorine. The condenser is no longer cooled, and the bulb destined to receive the crystals is immersed in a refrigerating mixture, which is connected with the apparatus by means of a caoutchouc tube lined with asbestos. The chlorine should pass very slowly, between 3 and 4 litres in twenty-four hours. However, the whole of the gas is not absorbed by the nitrate of silver. Some oxygen is given off, apparently very nearly equal in volume to the chlorine consumed. An apparatus thus arranged goes on day and night without any looking after. It is merely necessary to renew the supply of sulphuric acid which displaces the chlorine, the alcohol which feeds the lamp, and the freezing mixture.—*Comptes Rendus*, Feb. 17, 1849.

At a recent meeting of the Academy (March 5), M. Dumas communicated some further details concerning this highly interesting substance.

The tube containing the crystallized nitric acid exhibited to the members of the Academy having been left to itself became liquid. On attempting to make the substance crystallize again by means of a refrigerating mixture, the tube was destroyed with a violent detonation, owing to some accidental vibration. I suspect that the dry nitric acid was gradually decomposed into hyponitric acid and oxygen, and that the latter, from its state of compression, gave rise to the explosion. It is necessary therefore to handle this new product with precaution. Owing to this accident I am unfortunately unable to present to the Academy a very beautiful specimen of anhydrous nitric acid which M. Deville forwarded to me, the crystals of which were of considerable size, and from their beauty most readily admitted of the fundamental form of this substance being determined with certainty.

Chemical Examination of Sandal Wood. By Leo Meier.

The most recent investigation on this subject by Bolley* has shown that the colouring substance obtained by exhausting sandal wood,—1st, with alcohol and precipitating with water; and 2nd, by exhausting with potash, precipitating with muriatic acid, solution in alcohol and precipitation with water—from the paler kinds of wood was less oxidized than that from the darker kinds when prepared according to the first method; and that the pigment prepared

* Chem. Gaz., vol. v. p. 423.

according to the second, from paler wood, became more highly oxidized by treatment with potash. In the analysis of the lead compounds of the colouring principle, which were obtained by precipitating the alcoholic solution with acetate of lead, no accordant results were obtained; they appeared to be mixtures, on which account Bolley did not distinguish by name four substances which differed in their composition by the elements of water.

Meier distinguishes six different substances which may be extracted from sandal wood in part by alcohol and in part by water, viz. santalic acid and santalic oxide, which are contained in the alcoholic extract; and santalide, santaloide, santalidide and santaloidide, which are contained in the aqueous decoction of the wood.

Santalic Acid.—To obtain this the rasped wood is exhausted with æther; the reddish-yellow extract furnishes on evaporation to dryness, a mass of minute dark-coloured crystals, which have neither taste nor smell; this mass is repeatedly exhausted with boiling water, which thereby acquires a faint yellowish colour; or the rasped wood is exhausted with cold alcohol, evaporated to dryness, and the residue treated in the same manner as that obtained with æther. According to this the residue is perfectly soluble in æther and alcohol of 0·863 to 0·912 spec. grav. The alcoholic solution is precipitated with a solution of acetate of lead in alcohol; a dark violet santalate of lead falls, while the supernatant liquid retains a yellow colour. After frequent exhaustion with boiling alcohol the precipitate becomes nearly black. After being thus purified, the precipitate is suspended in alcohol and decomposed with sulphuretted hydrogen or sulphuric acid. A blood-red solution is obtained, which leaves santalic acid on evaporation.

Santalic acid is insoluble in cold and in hot water; it is of a beautiful red colour and is void of taste and smell. It separates from its solutions in microscopic prisms, dissolves in every proportion in alcohol of 0·863 spec. grav. and likewise in hot alcohol of 0·912; the concentrated solutions are of a blood-red colour, and in the diluted state yellowish; they redden blue litmus-paper. The solution in absolute alcohol is coloured dark violet by a few drops of a caustic or carbonated alkali, and leaves on filtration a dark violet powder upon the filter. The solution is apparently not altered by exposure to the air or to sunlight. The acid melts at 219° like a resin; but if the temperature be raised, it puffs up and begins to be decomposed, takes fire, and burns with a bright white flame, diffusing a very agreeable odour, and leaving a porous shining coal, which on incineration furnishes a gray ash, consisting of carbonate and sulphate of lime. When a metallic oxide is boiled with a solution of santalic acid, it acquires a red colour, of which it cannot be deprived by boiling alcohol of 0·863.

Concentrated sulphuric acid dissolves santalic acid of a dark red colour. Upon the addition of water the acid separates unaltered, but on the application of heat it is carbonized in the sulphuric acid solution.

When 1 part of strong nitric acid is added to 2 parts of a con-

centrated alcoholic solution of santalic acid, it does not change its red colour, but on boiling the mixture it becomes brown. When the liquid is evaporated nearly to dryness, no red vapours are given off, nor does anything separate. If the remaining liquid is mixed with cold water, a yellowish-brown powder falls, which after being washed with water has neither taste nor smell, is insoluble in æther and in water, but is readily dissolved by absolute alcohol and in alcohol of 0·863 spec. grav. When this acid liquid is saturated with barytic water, minute, yellow, deliquescent and tasteless crystals separate after the nitrate of baryta has been removed by crystallization; the minute crystals are insoluble in æther, soluble in water and alcohol.

Santalic acid completely neutralizes the alkalies; nearly all its salts are of a dark violet colour. The salts, especially those of the alkalies and of the alkaline earths, are soluble in water; the latter, however, but very sparingly in cold water.

On saturating a solution of santalic acid with caustic potash and evaporating, a potash salt is obtained as a dark violet mass, which is insoluble in æther and only sparingly soluble in boiling absolute alcohol, but much more so in boiling alcohol of 0·863 spec. grav. It dissolves readily in water. There is no deposit on solution. The solutions possess, in a concentrated state, a violet colour; if they are diluted so far that they become transparent, the colour passes into a red. The soda salt is obtained in the same manner, except that on saturating the acid solution with soda, the salt separates, and afterwards dissolves in pure water. The acid saturated with ammonia deposits on evaporation the acid free from ammonia.

Santalate of baryta and lime are obtained by saturating solutions of the acid with lime and barytic water. The salts of the earths and metallic oxides may be prepared by decomposing the santalate of potash.

Santalic acid does not dissolve with a red colour in æther, but with a yellow one, and in this solution no longer reddens blue litmus, and is not rendered turbid on being mixed with water. On evaporating the solution, the acid is left apparently unaltered.

Santalic Oxide is that substance, which, after removing the santalic acid by a spirituous solution of acetate of lead, remains dissolved in the solution of the ætherial or alcoholic extract of the sandal wood, and colours the solution yellow. This solution, after removing the excess of lead by sulphuretted hydrogen, furnishes, on evaporation to dryness, a shining yellow mass, which dissolves in alcohol of 0·863 spec. grav. A spirituous solution of acetate of lead again precipitates santalate of lead from this solution. If, on the other hand, the liquid is evaporated to dryness with the excess of acetate of lead, a violet residue is obtained, which communicates a yellow colour to boiling alcohol of 0·863, whilst santalate of lead remains undissolved. If the acetate of lead which the solution may still contain is precipitated by sulphuretted hydrogen, the liquid now no longer furnishes a violet precipitate with acetate of lead. This liquid is evaporated, boiled with water to remove any

acetic acid, dissolved in alcohol, and mixed with some caustic potash, when it instantly assumes a brown colour; on evaporation to dryness it leaves a brown mass, which has neither smell nor taste, and which, after it has been repeatedly exhausted with boiling water, is santalic oxide. It is a brown amorphous mass, unalterable in the air, somewhat viscous, and with neither taste nor smell; it dissolves readily with a brown colour in absolute alcohol and alcohol of 0·863, is insoluble in cold æther, and but very sparingly soluble in boiling. It is insoluble in hot and cold water. The solutions of santalic oxide are brown, have no action upon test-papers, and are rendered milky when mixed with water.

Sulphuric, muriatic, tartaric, oxalic and nitric acids change the brown colour of the solution instantly into a reddish-yellow without any deposit being formed. Santalic oxide dissolves with a brown colour when boiled with caustic potash; on evaporating the solution, a brown powder separates. When an acid is now added to the liquid, the powder separates together with unaltered santalic oxide, and the liquid becomes colourless. When the separated mass is treated with cold alcohol of 0·863, the oxide dissolves and the brown powder is left behind. Caustic ammonia and carbonate of potash also dissolve the santalic oxide with a brown colour. If a few drops of an acid, for instance tartaric or oxalic acid, are added to a solution of santalic oxide, its brown colour instantly passes into a yellowish-red. This solution still slightly reddens litmus-paper. When these solutions are evaporated to dryness, they furnish reddish-yellow residues, in which, after the uncombined acids have been removed by boiling with water, the acids may be detected by suitable reagents on solution in spirit. Nitric acid furnishes minute granular crystals, the other acids amorphous masses, which dissolve in æther and in alcohol of 0·793 to 0·912, are insoluble in water, and do not possess an acid reaction after the excess of acid has been removed from the dry compounds by means of water.

When santalic oxide is heated, it melts, diffusing a very agreeable odour, takes fire, and burns with a white flame, giving off white vapours. It leaves a porous cinder of a metallic lustre, which on incineration furnishes a gray ash consisting of sulphate of lime and some peroxide of iron.

Santalide and the other above-mentioned bodies, excepting santalic acid and santalic oxide, are contained in the aqueous decoction of the sandal wood. The santalide is obtained from the filtered solution by precipitation with acetate of lead. After washing the precipitate with cold water, it does not part with anything to hot water. It is suspended in alcohol and decomposed with sulphuretted hydrogen. The reddish-brown liquid filtered from the sulphuret of lead leaves an amorphous mass of the same colour. It is exhausted with æther, which, by dissolving some resin and a gallic acid (which strikes a black colour with perchloride of iron), acquires a yellow colour and leaves an insoluble residue. Hot water removes from this residue some santaloide and santalidide; what remains is santalide. This forms a dark red mass void of taste and smell; it does not dissolve

in hot or cold water when pure; but if it contain some santaloide, it is dissolved in small quantity with the santaloide. It dissolves readily in cold æther, in absolute alcohol, and in alcohol of 0·863 per cent. The solutions have a pure red colour, and do not redden blue litmus paper. The alcoholic solution furnishes with acetate of lead a very bulky chocolate-brown precipitate, and the liquid becomes colourless. Acetate of copper, dissolved in alcohol, changes the colour of the solution into brown without any deposit being formed even on boiling. Nitrate of silver and perchloride of iron behave in the same manner; no alteration is produced with the protochloride of tin nor with barytic or lime water; neutral carbonate of potash changes the colour of the solution on boiling into reddish-brown. Caustic potash and ammonia instantly change the colour to brown without any deposit being formed. Muriatic and dilute sulphuric acids produce no change; this is also the case with nitric acid. When heated, it puffs up without melting, leaves an easily incinerated cinder, and some ash consisting of peroxide of iron and carbonate of lime.

Santaloide is obtained by boiling the original aqueous decoction of sandal wood with carbonate of lead, which acquires a light brown colour, while the liquid becomes yellow. On evaporating the latter to dryness, it leaves a brownish-yellow mass, which on boiling with alcohol of 0·863 leaves a brown substance, apparently gum, while the yellow body is dissolved, and furnishes on evaporation a yellow substance in microscopic prisms. On dissolving this mass in absolute alcohol, a little more of a brown substance is separated; the solution, evaporated to dryness, leaves santaloide and santaloidide, the first of which is extracted with water.

The santaloide obtained by evaporating the aqueous solution is frequently redissolved and evaporated to purify it from santaloidide; the residue is dissolved in water until no more santaloidide remains and the solution does not furnish a brown precipitate with acetate of lead. In this state santaloide forms when dry an amorphous mass of a beautiful yellow colour, has a somewhat astringent taste and no odour. It is insoluble in æther, readily soluble in cold absolute alcohol, likewise in alcohol of 0·863 and in cold water. On solution it leaves a brown deposit.

These solutions furnish with metallic salts no very characteristic reactions; they are not altered, for instance, by acetate of lead, chloride of platinum and perchloride of iron, and have no reaction upon vegetable colours. Caustic and carbonated alkalies change the yellow colour into brown without producing any precipitate. The solutions of pure santaloide are yellow by transmitted and reflected light; but if they contain acetate of lead or lime, they appear blue when seen from the surface. Santaloide obtained by this method still left some lime on incineration; it puffs up when heated, and is carbonized without fusing.

Santaloidide is that which remains undissolved by cold water in the preparation of the preceding substance; it is repeatedly exa usted with boiling water to purify it. It then forms a dark brown

resinous mass, which is soft at the ordinary temperature and adheres to the fingers. It cannot be obtained in crystals. It is not altered in the air, has neither taste nor smell, is insoluble in æther, sparingly soluble in absolute, and readily soluble in boiling alcohol of 0·863 spec. grav. It is insoluble in cold and boiling water. On solution it leaves a brown sediment. The solutions are of a brownish-yellow colour; they have no action upon vegetable pigments, and furnish a brown precipitate with acetate of lead dissolved in alcohol. If the santaloidide contain no santaloide, the liquid above the precipitate is colourless; but if it contain santaloide, it is yellow. Caustic alkalies change the brown colour into red; acids alter the colour, but produce no precipitate. When heated, it melts like a resin, takes fire, and burns with a white flame. It leaves some ash on incineration.

Santalidide.—The aqueous decoction of the sandal wood is treated as for the preparation of santalide, when, as above observed, an aqueous solution of santalidide with some santaloide is obtained, which is separated by cold and not hot water. The solution is again precipitated with acetate of lead, when a precipitate is obtained consisting of a combination of oxide of lead with santalidide. This is decomposed with sulphuretted hydrogen, and the solution evaporated to dryness.

Thus prepared, santalidide forms an amorphous brown mass. It is insoluble in æther, as well as in absolute alcohol and alcohol of 0·863 spec. grav. It is very sparingly soluble in boiling alcohol of 0·912; it is very readily soluble in cold and in hot water. The solutions are brown, have no action upon vegetable pigments, and furnish a brown precipitate with acetate of lead; perchloride of iron separates a dark brown powder; caustic and carbonated alkalies merely render the colour darker; muriatic and nitric acids colour the solution yellow.—*Archiv der Pharm.*, lv. p. 285, *and* lvi. p. 41.

On the Atomic Weight of Mercury. *By* L. Svanberg.

Erdmann and Marchand's experiments, the result of which was the reduction of the former equivalent of mercury from 1265·8 to 1250·9, were based upon the estimation of the amount of mercury in a given weight of the peroxide. It may however be objected to these experiments, that either a minute quantity of undecomposed nitrate (from which the oxide had been prepared by ignition) was still mixed with it, or that in the decomposition of the nitrate at too high a temperature a minute quantity of metallic mercury or of protoxide may have been formed. These circumstances induced me to make a series of experiments on the subject, in the hope of ascertaining whether the method employed by those chemists deserved that confidence which must always be placed in numbers which have been deduced directly from experiments made on the oxide of the metal. In the following I shall communicate both those experiments which did not furnish me with any satisfactory result, and those on which in my opinion full reliance can be placed.

A. Instead of preparing the oxide of mercury by calcining the nitrate, I endeavoured to procure it by precipitating a hot solution of corrosive sublimate in large excess with caustic potash*.

The carefully-washed peroxide, prepared in this manner, dried at 302°, was reduced by hydrogen in a glass tube provided with two bulbs, when the mercury distilled from the one bulb into the other. So large an amount of foreign substance was left in the bulb which had contained the oxide, that it was quite evident the peroxide prepared in this manner could not be employed for the determination of the atomic weight of the metal.

B. The attempt to reduce the perchloride of mercury with hydrogen, in the hope that muriatic acid and metallic mercury would be formed, likewise failed; a large portion of the corrosive sublimate being volatilized with partial formation of calomel, and only a small portion of metallic mercury obtained.

C. On digesting a known weight of pure mercury with a large excess of distilled sulphuric acid, expelling the excess of acid and weighing the anhydrous persulphate of mercury, the result obtained was not more trustworthy, as the salt continually parts with sulphuric acid even at a temperature not exceeding 464°, becoming more and more basic. This, when calculated as neutral, gives an atomic weight for the metal which sometimes exceeds 1300.

D. By mixing a known weight of chlorate of potash with a known weight of calomel, then adding muriatic acid and heating the mixture, I conceived that I must obtain a good result, as the chlorate of potash would be reduced to chloride of potassium with evolution of chlorine, a portion of which would be absorbed to convert the protochloride of mercury into perchloride. From the weight of the mass evaporated to dryness the atomic weight of the mercury might be calculated, it being known from Marignac's experiments what amount of chloride of potassium is formed from a known weight of chlorate of potash. On employing this method, however, it was found excessively difficult to obtain a protochloride of mercury free both from perchloride and metallic mercury. It would also be excessively difficult to convert the whole of the protochloride into perchloride with quantitative accuracy.

E. I obtained no favourable result by precipitating a known weight of pure silver dissolved in nitric acid, because, as the experiment was made in the cold, a sparingly-soluble double salt of nitrate of mercury and nitrate of silver was formed, so that the precipitation of the chloride of silver was no longer perceptible to the eye, and so much corrosive sublimate was added as to indicate the number 1220 as the atomic weight. On warming the mixture, the double salt dissolves; but if the liquid is kept hot for any length of time, more and more chloride of silver dissolves in the acid solution of the nitrate of mercury, which is, it is true, again precipitated by a fresh addition of

* The sublimate used for these experiments had been previously sublimed in chlorine, to free it from a small admixture of the protochloride of mercury, which is constantly present. I have found that the protochloride is sparingly soluble in a solution of the perchloride.

solution of corrosive sublimate; however, this method is not applicable to the determination of the atomic weight. In some cases I added so much perchloride of mercury that the corresponding atomic weight rose to 1360. The solubility of the chloride of silver in a solution of the pernitrate of mercury had been previously observed by Prof. Wackenroder. I was however ignorant of the fact when making these experiments.

F. A known weight of corrosive sublimate was mixed with burnt lime, the mixture heated, and the mercurial gas passed over an incandescent mixture of caustic lime and powdered charcoal to decompose any admixture of the perchloride of mercury; it is requisite to mix a large excess of lime with the corrosive sublimate, otherwise the glass tube in which the operation is made readily cracks as soon as any fused chloride of calcium comes into contact with it. During the operation a constant current of hydrogen is passed through the tube in which the mixture is heated. In the hinder portion of the tube there is also a layer of caustic lime. The mercury which distils over is collected and weighed. I obtained in this manner the following results:—

12·048 grms. $HgCl^2$ furnished 8·889 grms. Hg, corresponding to the atomic weight 1247·33.

12·529 grms. $HgCl^2$ furnished 9·2456 grms. Hg, according to which experiment the atomic weight of mercury is 1248·21.

12·6491 grms. $HgCl^2$ furnished 9·3363 grms. Hg, which gives for the atomic weight of mercury 1249·27.

In these calculations, in which no correction for vacuum was made, I have assumed 443·28 as the equivalent of chlorine, according to the calculations made by Berzelius from Marignac's experiments. The mean of the three experiments gives us the atomic weight of mercury 1248·27, according to which the peroxide of mercury should contain 7·4106 per cent. oxygen, which differs from Erdmann and Marchand's determination only by 0·076 per cent.

I do not lay any great stress upon the numbers found by me; they however serve to confirm the number deduced by Erdmann and Marchand, as all the objections which might be raised against the method pursued by me point rather to a loss of mercury than otherwise. Since however the atomic weight proves under all circumstances to be lower the smaller the amount of mercury found in the experiment, the number obtained by me may perhaps deserve so much confidence that the atomic weight will not be admitted to be lower than 1248·7. Moreover, as I have not operated with larger quantities of mercury than $27\frac{1}{2}$ grms. taken altogether, whilst Marchand and Erdmann experimented with $352\frac{1}{3}$ grms., if the accuracy of the results should be judged of by the amount of weighed mercury, the above number will require very little alteration, on which account I consider 1250·9 to be the nearest expression of the results from experiments on the combining proportion of mercury. The question however cannot be considered as satisfactorily settled until it has been tested by some other method, for instance by the

determination of the amount of chlorine in the perchloride of mercury, of the sulphur in vermilion, or of some element in any other compound of mercury.—*Journ. für Prakt. Chem.*, xlv. p. 468.

On crystalline Phosphates of Lime and Protoxide of Manganese. By Dr. C. Bödeker.

Phosphate of Lime.—When a solution of chloride of calcium is precipitated with a slight excess of phosphate of soda, the liquid with the precipitate divided into two nearly equal parts, to one of which so much nitric or muriatic acid is added as is requisite to dissolve the precipitate in the cold, and the other half of the liquid, together with the precipitate poured into the acidified solution, and the whole set aside in the cold for forty-eight hours, it is soon observed that the amorphous precipitate of phosphate of lime is altered; it becomes heavier, and is gradually converted into delicate white laminæ, which when washed with water contain neither nitric acid, muriatic acid nor soda, but only lime, phosphoric acid and water. Frequently the plates are broader than usual, and then exhibit a very beautiful velvety lustre. Under the microscope they appear as thin, tabular, four-sided rhombic prisms, with the two sharp edges of the prism truncated, so that the salt generally occurs in irregular six-sided plates. It does not decrease in weight by drying over chloride of calcium or sulphuric acid.

The salt is decomposed by boiling with water; it becomes opake and indistinctly crystalline; at the same time a solution of biphosphate of lime, which strongly reddens blue litmus and is precipitated by basic oxalate of ammonia, is obtained. [When the salt is treated with cold water, it does not react upon blue litmus-paper.] The salt for analysis was dried over chloride of calcium. It gave—

Lime	32·56	..	2 =	703·30	32·60
Phosphoric acid..	41·22	(from the loss)	1	892·04	41·34
Water.....	26·22	25·89	5	562·40	26·06

4 atoms of the water were expelled at 302°, while the fifth required nearly a red heat. This behaviour and the above data lead to the formula $2CaO, HO + PO^5 + 4Aq$.

This salt has consequently the same composition as the concretions known under the name of Beluga calculi.

Phosphate of the Protoxide of Manganese.—By precipitating a solution of protosulphate of manganese with an excess of phosphate of soda, and partial solution of the precipitate in muriatic acid in the same manner as above for the lime salt, protophosphate of manganese is obtained in nearly colourless prisms, which have a faint tint of light red and possess a very strong vitreous lustre. On boiling with water, these crystals are decomposed, like the lime salt, into a soluble acid and an insoluble basic salt. Both salts fuse before the blowpipe with apparent ebullition, the first into a white opake mass, the latter into a dark brown globule.

The air-dried salt lost very little over chloride of calcium. As the absence of sulphuric acid, muriatic acid and of soda had been proved by a second examination, only the water and protoxide of manganese were determined, and the phosphoric acid ascertained from the loss. The salt lost at 230° 23·27 per cent. water=6 atoms, and 1 atom or 7·99 per cent. by subsequent ignition. The residue was dissolved in muriatic acid, mixed with some perchloride of iron and acetate of soda, and boiled; after the phosphoric acid had separated with peroxide of iron, the protoxide of manganese was precipitated with oxalate of potash and some carbonate of soda, ignited and weighed. The following are the results:—

Protoxide of manganese ..	34·86	2 =	889·37	34·62
Phosphoric acid	33·88	1	892·04	34·73
Water	31·26	7	787·36	30·65

And the formula is $2MnO, HO + PO^5 + 6Aq$.—Liebig's *Annalen*, Feb. 1849, p. 208.

On Caprylone. By G. Guckelberger.

As far as experience goes respecting the behaviour of the volatile acids of the series $(C^2H^2)^n + O^4$, on dry distillation of their combinations with the alkalies and the alkaline earths, it may be admitted that they are decomposed, with the elimination of 1 equiv. CO^2, into substances which contain the remainder of the C, the whole of the H and a third of the O of the decomposed anhydrous acids, without therefore any separation of carbon. The following experiments furnish a further proof of this decomposition, so peculiar to the acids above-mentioned. Only a small number of the acids mentioned have been examined in this respect; the products of acetic and margaric acids are best known; those of butyric and valerianic acids have only been described within the few last years by Chancel; to this series belongs caprylone, a description of which will prove an interesting addition to our knowledge of these bodies.

The caprylic acid was obtained from cocoa-nut oil; the baryta salt employed for the experiments was pure, as an estimation of the baryta showed. The decomposition which the volatile acids of the series in question experience does not exclusively take place in so simple a manner; in most cases there is a separation of carbon and the formation of various volatile products, which point to a more complicated process of decomposition. This second process, as the experiments with caprylate of baryta have shown, may be almost entirely prevented by taking, instead of the pure salt, a mixture of it with an excess of hydrate of lime, and distilling it carefully, so that the entire mass of the mixture is raised as quickly as possible to the suitable temperature.

By distilling caprylate of baryta alone at a temperature which was raised gradually to a faint red heat, a residue containing much eliminated carbon, and a distillate which consisted of acid water and a yellow oil with the odour of acetone floating upon it, were obtained.

After some time some white flakes separated from the oil; the oil therefore was a solution of a solid substance in one or probably several liquid substances. The great amount of carbon which separated showed distinctly that the decomposition of the acid had not taken place in so simple a manner as was expected; and the subsequent experiments were principally made with the object of discovering a plan by which the separation of carbon might be prevented, and the decomposition thus rendered more simple. The most favourable results were obtained by heating quickly to a faint red a mixture of half an ounce of caprylate of baryta with one ounce of hydrate of lime in a hot retort with a flat bottom over a charcoal fire. With the quantities above given the distillation was completed in from twenty-five to thirty minutes. During the operation heavy white vapours were disengaged, which condensed into a yellow oily liquid in a receiver kept cool by means of water, but which after a short time congealed to a yellow mass of the consistence of butter. By pressure between numerous folds of bibulous paper, a dark yellow liquid was removed, leaving behind a white crystalline mass, the melting-point of which was 95°, and which on being burnt with oxide of copper furnished 77·39 C, 13·15 H, 9·46 O.

As these numbers agree so closely with the formula $C^{15} H^{15} O = C^{16} H^{15} O^3 - CO^2$, it was not doubted that the crystalline substance obtained was the expected product of caprylic acid. The difference between theory and experiment arose, as was evident, from some impurity which could be removed by washing with cold alcohol, and then crystallizing from hot alcohol; the substance so purified melts at 104°. Pure caprylone is perfectly white, and most resembles Chinese wax in its crystalline structure; it is tasteless, has a faint waxy odour, is lighter than water, but sinks in alcohol of 0·890; it is insoluble in water, and floats upon it in a melted state as a colourless oil; it dissolves readily in æther, fatty and essential oils, and also in cold alcohol of 0·863 per cent., in considerable abundance, so that on recrystallization a considerable loss is frequently experienced; it dissolves in such quantity in boiling alcohol and pyroxylic spirit, that the whole solidifies to a pasty mass on cooling. Caprylone crystallizes from these solutions in fine silky needles; it melts, as above stated, at 104°, but solidifies at 100° to a radiately-crystalline mass; at 352° it boils, and distils without decomposition.

Caprylone, purified by repeated crystallization from alcohol, and burnt with oxide of copper with some chlorate of potash at the end of the tube, gave the following results:—

Carbon	79·08	79·27	15 =	90	79·64
Hydrogen	13·41	13·23	15	15	13·27
Oxygen	7·51	7·41	1	8	7·09

Caprylone is not altered by potash nor by nitric acid, even fuming, at the ordinary temperature, whilst an acid of 1·4 spec. grav. acts very violently upon caprylone at the temperature at which it is liquid. If the vapours which escape are passed through water, this acquires an ætherial odour, and the caprylone is decomposed into a dark

yellow oily liquid, which is heavier than water and scarcely soluble in it; it can consequently be freed from adherent nitric acid by washing it with water. The washed liquid possesses a burning aromatic taste; it dissolves readily in aqueous solutions of the alkalies; its solution in ammonia gives a deep yellow precipitate with salts of silver and of lead; the silver salt is rapidly decomposed even under the air-pump, and deflagrates at a gentle heat. This substance is consequently analogous to that which Chancel obtained from butyrone with nitric acid, and may receive the corresponding name of *nitrocaprylic acid.*

Unfortunately, from want of material, no experiments could be made to decide the question, whether the acetones contain a number of equivalents divisible by 2. This question has been touched upon by Chancel in his investigation of valeral and valerone*; he was induced to express the composition of valerone by the formula $C^{18} H^{18} O^2 = 2(C^9 H^9 O) = C^{10} H^{10} O^2 + C^8 H^8$, therefore as a combination of the aldehyde of valerianic acid with a hydrocarbon (butyrene). Chancel also expresses the opinion, that the acetones in general have a similar composition. If this view is correct, of which however no proofs are given, caprylone would be $2(C^{15} H^{15} O = C^{30} H^{30} O^2 = C^{16} H^{16} O^2$ (aldehyde of caprylic acid) $+ C^{14} H^{14}$ (œnanthylene). The correctness of this formula might perhaps be proved by ascertaining the density of the vapour; its boiling-point is not in its favour.

The oily product of decomposition of caprylic acid was not submitted to more accurate investigation, on account of the small quantity rendering it impossible to purify it; some reactions however showed that it contained a body belonging to the class of the aldehydes; for example, caustic potash gave rise to the production of a brown substance, and a solution of silver and a little ammonia furnished a mirror on the application of heat. Pure caprylone does not possess these properties, so that it is very easy to detect a trace of the oily substance in it by means of a solution of caustic potash and solution of silver.—Liebig's *Annalen,* Feb. 1849.

On the two new Organic Alkaloids, Methylamide and Ethylamide.

At a recent meeting of the French Academy, M. Dumas gave some further details relative to the interesting discoveries of M. Wurtz, described in our last number. The first alkaloid that corresponds to the methylic series $NH^2 C^2 H^3$ is a permanent gas; it is colourless, equally alkaline as ammonia, and like it very soluble in water; it is absorbed in considerable quantity by charcoal, and fumes in contact with the vapours of hydrochloric acid. It combines instantly with hydrochloric acid gas, forming a colourless crystalline compound. The two bodies unite in equal volumes. The hydrochlorate thus obtained readily furnishes the gas when acted upon with alkalies. All these characters are so identical with those

* Chem. Gaz., vol. iv. p. 133.

of ammonia, that it is highly probable the new alkali has been frequently mistaken for it; however it differs from it by its odour, which, while being ammoniacal, at the same time resembles that of salt water. But it differs essentially in being inflammable, burning with the production of carbonic gas and a pale yellow flame like that of the nitrogenous æthers, and in general of those inflammable substances containing nitrogenous compounds excepting cyanogen.

The alkali $NH^2 C^4 H^5$ has not been obtained in the gaseous state; it forms a highly volatile liquid, which begins to boil at the temperature of the hand; it fumes in the presence of acid vapours, and takes fire in contact with the air and any substance in a state of combustion.

M. Wurtz hopes soon to be able to produce some of the alkalies belonging to the hydrocarbons, holding a higher position in the series.

On a new Product of the dry Distillation of Amber.
By L. F. Bley *and* E. Diesel.

This substance, which resembles wax, was obtained in some experiments variously modified in order to obtain the largest possible amount of succinic acid from amber. In one of these experiments 32 oz. of amber were mixed with 2 oz. of crude concentrated muriatic acid, which had been previously diluted with an equal amount of water, and submitted to distillation in a glass retort. By accident a very brisk fire was made. When the operation was finished, a yellow wax-like substance was found in the neck of the retort mixed with the sublimed succinic acid. A somewhat loose cinder remained in the retort instead of the colophony; it weighed 3 oz., whilst the quantity of oil was very considerable, viz. $21\frac{1}{2}$ oz.; whilst in the usual mode of distilling, generally only between 4 and 5 oz. of oil are obtained from 16 oz. of amber. The amount of succinic acid was $1\frac{1}{2}$ oz.

The wax-like substance was well washed and purified by being melted in water and solution in absolute alcohol. In thin layers it is yellowish, in large masses brownish-green, lighter than water, soft, transparent or opake, melting between 185° and 187°, and boiling somewhat above 572°, and void of taste and smell. It is insoluble in water, readily soluble in alcohol and æther, fats and liquid oils, and burns with a strong luminous flame. The analysis of the substance dried over chloride of calcium furnished—

Carbon	86·123	1 =	6	85·7
Hydrogen	13·691	1	1	14·3

From the properties and composition of this substance, it agrees with a body found near Merthyr Tydvil, in England, in narrow veins, with quartz, calcareous spar and iron ores, at Loch Fyne in Scotland, and at Seamick in Moldavia in layers of bituminous schists, and is described with the same properties by Oken under the name of ozocerite (Hatchetine). The authors however are of

opinion that the muriatic acid used for these experiments has no influence on the production of this wax-like substance, which the authors have provisionally called artificial ozocerite.—*Archiv der Pharm.*, lv. p. 171.

ANALYTICAL CHEMISTRY.

On the Estimation of Chromium. *By* Dr. H. Schwartz.

The extensive use of the preparations of chromium in the arts, their frequent adulteration, and the variable composition of the principal source, chrome-iron ore, renders it important that a simple method of estimating chromium should be substituted for the complicated and not very accurate methods now in use. The method hitherto employed consisted either in precipitating the chromic acid by acetate of lead in the state of chromate of lead, or throwing it down in the form of oxide of chromium. The first is somewhat soluble in water, the second difficult to free from alkali. Vohl* oxidizes all the chromium into chromic acid by passing chlorine into an alkaline solution when it is in the state of oxide, evaporating and destroying the admixture of chlorate of potash by heat. He then transfers the chromate of potash into the apparatus of Will and Fresenius, adds oxalic acid, and finds the amount of expelled carbonic acid exactly as in the analysis of manganese. The equation $2CrO^3+3C^2O^3=Cr^2O^3+6CO^2$ gives the amount of chromium present.

The method which I propose is as follows:—The whole of the chromium must be converted into chromic acid; and when oxide of chromium is present, this must be oxidized by fusion with hydrate of potash and chlorate of potash. This chromic acid is most readily and quickly reduced according to the formula

$$6FeO+2CrO^3=3Fe^2O^3+Cr^2O^3.$$

When I have taken a known quantity of FeO, which must be in excess, and now determine, according to Marguerite's† method, by the addition of a normal solution of permanganate of potash until the red colour no longer disappears from reduction, the remainder of unoxidized FeO, the difference between the FeO left and that consumed gives the amount of FeO oxidized by the CrO^3, and consequently the amount of Cr, Cr^2O^3 or CrO^3. It results from the above formulæ that 1·000 Fe corresponds to 0·3143 Cr, 0·4571 Cr^2O^3, and 0·600 CrO^3.

We might also weigh off 2·100 grms. iron, which would require for oxidation 100 cubic centimetres of permanganate of potash; and if we desire to know the

Cr	in per cent.,	weigh off	0·660	grm. substance.
Cr^2O^3	...	...	0·960	...
CrO^3	...	...	1·260	...

* Chem. Gaz., vol. vi. p. 21. † Ibid., vol. iv. p. 216.

If now *a* vol. (cub. cent.) solution of permanganate of potash had been consumed for completing the oxidation, the substance under examination contained $100 - a$ per cent. Cr, Cr^2O^3, CrO^3, according as 0·660 grm., 0·960 grm., &c. were weighed off. I now proceed to describe the mode of operating. 2·100 grms. iron are weighed off, and dissolved in hydrochloric acid, or in its stead a solution of protosulphate of iron measured or weighed off, the amount of iron in which is known, and which should exactly contain 2·100 grms. Fe. The solution does not become oxidized so readily as is generally believed when it is sufficiently acid and preserved in well-closed bottles. Thus, for instance, 25 cub. cent. recently-prepared solution of iron required 25 cub. cent. permanganate of potash. After six weeks, during which time the bottle had been frequently opened, they still required 25 cub. cent. permanganate of potash for oxidation; but the chameleon had slightly deteriorated, for on further measuring off 25 cub. cent. solution of iron and reducing it by zinc, 25·2 cub. cent. permanganate were required.

Now when the chromic acid of a salt, &c. is to be determined, 1·260 of it is added to this acid and very dilute solution of iron, after having removed any bases contained in the substance, that are precipitated by muriatic or sulphuric acid, and so obtained a clear solution of chromic acid. A lively grass-green colour is instantly perceptible if the protoxide of iron was in excess; otherwise frequently the brown $Cr^2O^3 + CrO^3$ falls. The different oxides of chromium and their salts are finely pulverized, and employed when possible in the anhydrous state, in order to avoid any frothing and effervescence in the following operation.

With chrome-iron ore, $FeO + Cr^2O^3$, of which the different fragments may vary considerably in composition, an average sample is taken, as in the case of chloride of lime, and reduced to an extremely fine powder. Solid hydrate of potash, as free as possible from water, is conveyed into a crucible of chemically-pure silver, and heated until it forms a perfectly oily liquid; the flame is now moderated, and 0·960 grm. substance added when it is desired to determine the per-centage of Cr^2O^3. As soon as this is completely moistened by the potash, small fragments of fused chlorate of potash are added, and the flame now carefully regulated.

A violent effervescence results from the escape of oxygen; at the same time the mass becomes more and more yellow; and when the whole of the chlorate of potash is decomposed, it becomes clear and transparent, so that the bottom of the crucible is perceptible. The crucible is let cool, placed in a beaker, and hot water poured over it, then carefully removed, rinsed and set aside; the liquid is allowed to cool, and then supersaturated with muriatic or sulphuric acid until it appears of an orange colour.

If the temperature has not been too high, there is no fear of any disengagement resulting on the addition of ClH. No attention need be paid to a few black flakes, which are merely traces of metallic silver from the crucible.

CrO^2Cl or $2CrO^3 + CrCl^3$ is enclosed in glass tubes, weighed, and these broken under the liquid.

I now add the solution of permanganate of potash from a burette to the solutions, which contain besides Cr^2O^3 and Fe^2O^3 some FeO. The green colour of the liquid does not mask the red of the chameleon; on the contrary, it appears as if the contrast of the complementary colours facilitated the comparison. In order not to waste too much chameleon, I have frequently, when the probable amount of CrO^3 or Cr^2O^3 was known to me, taken very little more iron than was exactly requisite, and have completed the operation by decimal solutions of permanganate of potash.

Admixtures of substances which do not become oxidized have no influence upon the analysis. Of other substances—

a. ClO^5 may be destroyed by heat.

b. NO^5 does not act in the cold, when in a very dilute state, upon FeO.

c. The NO^3, which is readily formed on fusing Cr^2O^3 with KO, NO^5, proved rather annoying at first; it oxidizes the FeO, and nevertheless instantly reduces CrO^3 in an acid solution. I finally succeeded in removing it by boiling the alkaline solution with chloride of ammonium until it had a neutral reaction; there is then produced $NH^4O + NO^3$, which is already decomposed at 122°, in neutral liquids, into N and HO.

d. Manganic acid is likewise destroyed by boiling the alkaline solution with chloride of ammonium; MnO^2 separates, which is removed by filtration.

e. If any ferric acid were formed, it would be destroyed on the addition of hot water.

The method was tested upon bichromate of potash, neutral chromate of potash, chromate of baryta, chromate of the protoxide of mercury, chromate of the perchloride of chromium, oxide of chromium and chrome-alum, with very excellent results: further, on a chrome-iron ore, which furnished 36·2 to 36·4 per cent. oxide of chromium, and chrome ochre from Halle, which gave 1·9 to 2·1 per cent. oxide of chromium when analysed in the same manner.—Liebig's *Annalen*, Feb. 1849, p. 210.

On a new Method of estimating Phosphoric Acid by means of a Normal Solution. *By* E. Cottereau.

It is well known what an important part phosphoric acid plays in the development of animals and plants, and how essential it is that physiologists and agriculturists should be able to determine the proportion in which it exists in soils, manures and nutritive substances. The usual methods of estimating this acid however are very tedious and difficult; perhaps the following process, which I have found to give excellent results in several analyses of manures, will prove useful.

The method proposed is based, first, on the property possessed by solutions of potash and soda of converting the insoluble phosphates

by ebullition into soluble phosphates of potash or soda; and secondly, on the property which the nitrate of silver has of precipitating the phosphates of potash or soda, yielding a phosphate of silver the composition of which is represented by the formula $2AgO, PO^5$, and which is deposited the more readily the nearer the precipitation approaches to completeness; a peculiarity which enables us to seize the moment the reaction is finished. The following is the plan of proceeding.

A known weight of the insoluble phosphate or phosphates* is boiled for some time with four times as much pure carbonate of soda in 8 to 10 vols. of distilled water. Phosphate of soda and an insoluble carbonate are formed; the latter is separated by filtration and the filter washed twice with boiling distilled water. The liquid is well mixed, and a quantity of pure nitric acid added to saturate the excess of carbonate of soda; it is then divided into two equal portions, which are placed in two separate test-glasses; and then to these portions of liquid the normal solution of nitrate of silver is added by cubic centimetres, each cubic centimetre representing a known weight of oxide of silver. The solution I have employed is prepared by dissolving 48·57 grms. pure fused nitrate of silver in 1 litre of distilled water; so that 1 cubic centimetre of the solution represents 0·04857 hundred-thousandths of nitrate of silver, corresponding to 0·01 centigramme of phosphoric acid. The liquid is agitated, and then another cubic centimetre of the test-liquor added; the whole again stirred, and the addition of test-liquor continued until the liquid becomes perfectly clear after a little rest, which only takes place as above stated when the saturation is complete. Now each cubic centimetre of the normal solution which has been employed represents 1 centigramme of phosphoric acid; and with a little practice we are able to find the proportion of this acid to within one half-hundredth.

If we have to analyse a manure containing soluble and insoluble chlorides and sulphates along with the insoluble earthy phosphates, the first operation is to ascertain the quantity of soluble salts which exist in a given weight of the substance. The chlorides are thus eliminated by this operation, and there is no danger of any chloride of silver being formed in precipitating the phosphoric acid. Sometimes however it happens that soluble phosphates are contained in the substance which accompanies the other soluble ingredients; but it is very easy to convert them into insoluble phosphates without affecting the chlorides. A second determination gives the quantity of phosphoric acid which they contain. I may observe that the silicates do not at all interfere; and lastly, that the precipitates of phosphate of silver may easily be converted by carbonate of soda into carbonate of silver, and this again into nitrate.—*Comptes Rendus*, Jan. 22, 1849.

* The soluble phosphates may always be converted into the insoluble state by double decomposition.

PATENT.

Patent granted to Moses Haym Picciotto, Finsbury-square, London, *for a method or methods of purifying and decolorizing certain Gums.*

This invention consists in two processes for purifying and decolorizing all varieties of gum-arabic, including that brought from Senegal.

The first process is as follows:—The patentee prepares a rather strong solution of sulphurous acid gas, and purifies the gas previously to using it by passing it through water contained in a suitable apparatus. The purified acid solution of the gas must be protected as much as possible from the contact of atmospheric air. Into the solution a quantity of gum-arabic, in the state in which it is imported or in powder, is introduced in the proportion of 1 part by weight of gum to from 6 to 12 parts of the solution. When the gum is dissolved, it will be found that the greater portion of its colouring matter has been destroyed, or has chemically combined with the sulphurous acid, forming a colourless compound. The sulphurous acid may be brought into contact with the gum by other methods than that just described; for instance, if a current of the purified gas be introduced into a solution of the gum, it will be readily absorbed; or the sulphurous acid gas may be introduced into a close receiver, surrounded with some refrigerating substance, wherein, by the action of cold and the pressure of the gas itself, it will be condensed into a liquid form, and in this form may be mixed with a solution of gum.

In order to separate the acid, or the acid combined with colouring matter, from the solution of gum, various methods may be adopted, but the patentee prefers the following:—He applies heat for a short time to the close vessel containing the mixture, during which time the portion of gas evolved may pass through a tube into another receiver containing water, and thus be recovered for another operation; and then he allows the hot mixture to run off in small portions into a larger and open vessel containing (rather in excess) some salifiable base, which in its combination with sulphurous acid will form an insoluble salt. Various substances may be used for this purpose, but the patentee prefers carbonate of baryta, as sulphite of baryta is an absolutely insoluble salt as well as the sulphate. The combination is aided by stirring; and when the whole of the disengaged carbonic acid gas has been driven off and the solution becomes neutral, the vessel is covered and the solution allowed to rest for some hours, so that the coarser parts of the solid matters may be deposited. The neutralization of the acid may also be effected without previously heating the liquid; but then the patentee recommends that it should be heated after the combination has taken place, in order to drive off all carbonic acid, which, if allowed to remain in the solution, would dissolve a small portion of undecomposed carbonate of baryta. The solution is now to be filtered, in order to separate the insoluble sulphite of baryta and other insoluble impurities therefrom. The patentee prefers to effect the filtration through

a thin layer of pure gelatinous hydrate of alumina (which may be obtained by the decomposition of sulphate of alumina) laid on cloth; or the same object may be effected by forcing the pure liquid through unglazed earthen- or stone-ware. After the solution has been filtered, it will be found that all ligneous fibre, sand and earthy matters, and all particles of insoluble gum, have been separated from the solution, and deposited in the vessels used and on the filter with the sulphite of baryta, and very little colour will remain in the filtered solution; but when a very white gum is required, the process of acidulation must be repeated. By evaporating the filtered solution, a colourless, tasteless and pure gum is obtained, the natural properties of which have not been altered in the least degree.

The sulphurous acid gas may be separated from the solution of gum, without neutralizing it by means of a base, by boiling the mixture in a close air-tight vessel, and conducting the gas which is driven off into a receiver containing water. If required, the decolorizing process may be repeated, by introducing a current of pure sulphurous acid gas into the vessel containing the solution, and then separating it by ebullition. When the solution has become cool, it will be found that all the impurities originally united with the gum are deposited at the bottom of the vessel, and the pure solution may be drawn off; or the whole contents of the vessel may be emptied into cloth bags, and the solution allowed to filter through the same.

The second process for purifying gum-arabic is as follows:—The gum is dissolved in cold or hot water, in the proportion of 1 part by weight of gum to from 6 to 15 parts of water, and the solution is filtered through cloth; then a quantity of pure gelatinous hydrate of alumina, or hydrate of alumina containing a small portion of fine pipe-clay or other earthy and insoluble substance, is thoroughly mixed with the solution, with or without heat, so as to form a homogeneous compound of about the consistence of thin paste; and this being now filtered through cloth, the pure solution of gum that percolates through will be found greatly decolorized. Instead of making the mixture just described, the simple solution of gum may be passed through a bed of alumina, or alumina and other substances, and the decoloration will be effected equally well; but then the filtration must be much slower. The filtered solution must be again operated upon with a fresh portion of hydrate of alumina (alone or with other substances) if a perfectly white gum is required, and sometimes a second repetition of the process may be necessary; but as the second and third portions of alumina, after being used, contain very little colouring matter, they may serve again for the first decolorization of another portion of gum. When the hydrate of alumina (alone or with the other substances) is highly charged with colouring matter, it is washed with hot water on the filter to separate the adhering gum from it; after which the alumina is washed with a cold aqueous solution of chlorine or with a limpid solution of chloride of lime; and then it is filtered and again washed repeatedly with hot water. Its original whiteness and purity are thus restored, as well as its chemical affinity for colouring matter.—Sealed August 17, 1848.

THE CHEMICAL GAZETTE.

No. CLVI.—April 16, 1849.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On some Substances derived from the Menispermeæ.
By Dr. Bödeker.

Wittstock prepared columbine from *Cocculus palmatus*, DeC. The author obtained it more readily and in a purer state by exhausting the Columbo root with spirit of 0·876 spec. grav., removing the spirit and rendering the residue as dry as possible. This residue is dissolved in water, and an equal volume of æther added, the two liquids frequently shaken, the separated æthereal solution removed with a siphon, filtered, and the greater portion of the æther separated by distillation. The aqueous solution of the Columbo extract is treated repeatedly with æther until this dissolves scarcely anything further. The æther takes up, besides the columbine, a fatty oil, the greater portion of which remains dissolved in the little æther not distilled off. The greater portion of the columbine soon separates from this residue in a crystalline state. After pouring off the oily mother-liquor, which still contains columbine, the crystalline mass is rinsed with cold æther, and then pressed between folds of bibulous paper. It has still a yellow colour, and must for further purification be dissolved in boiling æther containing neither alcohol nor water, and the æther distilled off to one-fourth, when most of the columbine separates perfectly white, whilst the fat remains dissolved with the remainder of the columbine. It is difficult to remove this fat entirely from the columbine, which however succeeds by frequent recrystallization. The presence of fat may readily be detected on dissolving the columbine in acetic acid when it floats in drops in the liquid.

The composition of columbine is represented by the atomic relations $C^{42}H^{22}O^{14}$. No combination of it could be obtained, on which account the formula with 42 atoms of carbon was merely assumed for the reason that the same number is contained in the following substances procured from the Columbo root; and these, as will be subsequently shown, are closely related to each other. Metallic salts do not precipitate columbine. Emulsine has no effect upon columbine mixed into a paste with water. An experiment to obtain a product of decomposition by fusion with aqueous potash, which might have thrown some light upon the composition, was not attended with success, for in the presence of a sufficient quantity of

water the columbine is dissolved unaltered, whilst it is entirely decomposed when less water is present; in the latter case acids precipitate a brown humus-like substance from the aqueous solution of the fused mass. The numbers obtained by the author on analysis differ somewhat from those of Liebig, which is probably owing to the substance prepared by Wittstock, and analysed by Liebig, having been less perfectly separated from the fat. The analysis gave—

Carbon.....	65·11	65·29	42 =	3155·04	65·33
Hydrogen....	5·95	6·01	22	274·56	5·68
Oxygen.....	28·94	28·70	14	1400·00	29·09

Berberine, $C^{42}H^{18}NO^{9}$*.—We noticed, in a former Number of this Journal (vol. vi. p. 302), the discovery of this substance by the author in the root of the Columbo. The dry spirituous extract of Columbo, exhausted with hot lime-water, furnishes a deep brown-red solution, which on saturation with muriatic acid deposits an almost wholly amorphous substance mixed with a few yellow crystalline particles. After filtration, an excess of muriatic acid is added, when in the course of a few days an abundant crystalline deposit is formed. The mass, which still has an acid reaction, is dissolved in alcohol of 0·850, again precipitated and washed with æther. In this manner the berberine was obtained in the form of a beautiful bright yellow powder, which under the microscope presented the appearance of a confused aggregation of crystals. The aqueous solution, which was not acid, indicated the presence of a considerable amount of chlorine; gave with tannin, chloride of platinum, perchloride of mercury, chlorate and chromate of potash, amorphous yellow precipitates; muriatic, nitric and sulphuric acid, on the other hand, furnished crystalline deposits of different forms, which however all possessed the properties assigned by Fleitmann to the muriate of berberine. The author's analysis of the muriate of berberine from Columbo root likewise agrees with that of the muriate of berberine, $C^{42}H^{18}NO^{9}$, HCl, HO, from the barberry by Fleitmann:—

	Fleitmann.		Bödeker.
Carbon	62·89	62·53	62·78
Hydrogen	5·44	5·67	5·07
Chlorine.....	9·13	8·80	9·06

According to the observations of the author, berberine furnishes quinoline on distillation with milk of lime and the hydrated oxide of lead.

The occurrence of this substance in *Berberis* and *Cocculus* is remarkable in a physiological point of view. Bartling places both these families, the *Menispermeæ* and *Berberidæ*, in the class of the *Cocculinæ*, which is in accordance with the fact of both containing the same principle. The columbine occurs in the cells of the root in the crystalline state; the berberine, on the contrary, is deposited in the yellow thickening layers of the cell-membranes mixed with a fatty substance, which protects it from the solvent action of the

* Fleitmann in Chem. Gaz., vol. v. p. 129.

alcohol when the root is treated with this agent. Berberine occurs in *Berberis vulgaris* in precisely the same manner, except that it is deposited more abundantly and in a purer state. All the cells, and especially the vessels and woody cells, exhibit broad golden-yellow thickening layers, in which the berberine is very easily detected under the microscope; for on mixing a drop of muriatic, sulphuric or nitric acid with a drop of absolute alcohol with which the root has been treated, the corresponding salt of berberine immediately begins to crystallize upon the slip of glass. The author draws especial attention to the circumstance, that the berberine is found in cells, and not in peculiar organs of secretion. That it does not exist in the free state in the Columbo root is evident from the properties of the yellow crystalline masses which separate with the columbine from an inspissated alcoholic extract. The neutral reaction, and in comparison with berberine less solubility in water and lighter golden-yellow colour, sufficiently prove it to be a salt of berberine. Acids separate from its solution in water, and still better in lime-water, columbic acid; whilst but relatively very small quantities of potash are contained in the form of chloride of potassium and nitre in these impure deposits; consequently the berberine can only be contained in the thickening layers of the cells of the Columbo as columbate of berberine. It appears to exist in a different form in *Berberis* according to the author.

Columbic Acid, $C^{42}H^{23}O^{13}$ (dried at 239°).—The solution obtained on digesting the dried alcoholic extract of Columbo with lime-water, and the turbid aqueous solution of the spirituous extract of Columbo, deposit on the first addition of acids, before the separation of any berberine salt, more or less purely amorphous yellow precipitates. They are washed with water to remove any salt of berberine. By exhaustion with boiling æther, the columbine is removed, upon which it is dissolved in dilute caustic potash, and carbonic acid passed into the solution, which precipitates a dark brown flocculent substance. A slight excess of muriatic acid now throws down a copious white flocculent precipitate, which during the washing upon the filter condenses into a pale straw-coloured powder without any signs of crystallization. The acid thus obtained burns with flame when heated upon platinum foil, leaving no residue; it was free from muriatic acid, and had a strong acid reaction upon moist litmus-paper. Its taste is bitter, like that of columbine, but less so. It dissolves but sparingly in cold æther, scarcely at all in water, more readily in acetic acid, but best of all in alcohol, with a light yellow colour. Cold nitric acid has no action upon it; even concentrated sulphuric acid dissolves the substance apparently unaltered at a gentle heat; upon the addition of water it appears to be thrown down unaltered; it readily dissolves in dilute caustic potash with a light brownish-yellow colour. Its alcoholic solution is not precipitated by acetate of copper; with an alcoholic solution of acetate of lead it furnishes a copious yellow precipitate. From all the solutions in alcohol, æther and acetic acid, the columbic acid was constantly obtained in the form of a yellow varnish-like residue.

The pure acid and a basic lead compound (the precipitate produced by an alcoholic solution of acetate of lead in the alcoholic solution of the acid) were employed to determine the composition. The lead salt, after being dried at 212°, lost up to 266° 4·29 per cent. of water. The salt dried at 212° contained 30·19 per cent. oxide of lead. The acid dried at 104°, heated to 239°, lost 5·04 per cent., of which however half was expelled at 212°. The acid dried at 239° gave—

Carbon	66·64	42	= 3155·04	66·54
Hydrogen	6·29	23	287·04	6·05
Oxygen	27·07	13	1300·00	27·41

We have therefore—

Anhydrous acid in lead salt dried at 266° = $C^{42}H^{21}O^{11} = \overline{Col.}$

Acid dried at 104° ..... $C^{42}H^{21}O^{11} + HO + 3aq.$

Acid dried at 212° ..... $C^{42}H^{21}O^{11} + HO + 2aq.$

Acid dried at 239° ..... $C^{42}H^{21}O^{11} + HO + aq.$

The analogy of these three substances occurring in the Columbo root, with three others also contained in a Menispermeaceous plant, the *Anamyrta Cocculus*, is remarkable. We have, on the one hand, columbine, columbic acid and berberine, and on the other, picrotoxine, cocculinic acid (subpicrotoxic acid) and menispermine. The latter basic substance occurs, according to Peltier and Couerbe, with the acid in the highly vascular shells, whilst the neutral picrotoxine is deposited in the inner parenchyma of the kernel, which is nearly destitute of vessels. According to the author, exactly the same occurs in the Columbo root; the base and the acid are found most abundantly in the thickening strata of the vessels and the adjacent cells, whilst the cells of that portion of the parenchymatous tissue in which no formation of vessels has yet commenced contain extremely little or no berberine, but are filled with neutral columbine. Now it appears probable that columbine was likewise produced in the older cells (which subsequently become situated in the interior of the root and are permeated by vessels), when they possessed the same relative position as those layers which at present contain columbine; hence it may be admitted that the neutral substance must be considered to be the relatively primary formation, which subsequently, with the development of the vascular tissue, and the addition of ammonia as conjunct, became separated into an acid and a base. Even should we not be disposed to lay too much weight for the present on this view, it will still serve to exhibit the formation and connexion of the substances occurring in the Columbo root:—

2 equivs. columbine..	$C^{84}H^{44}O^{28}$	Berberine	$C^{42}H^{18}O^{9}N$
1 equiv. ammonia ..	$H^{3}N$	$\overline{Col.} + 8HO$ ..	$C^{42}H^{20}O^{19}$
	$\overline{C^{84}H^{47}O^{28}N}$		$\overline{C^{84}H^{47}O^{28}N}$

The author has also prepared and analysed the alkaloid *Pelosine*, discovered by Wiggers in the root of an American Menispermea,

Cissampelos Pareira, Lam. It was prepared according to the same method, and possessed the properties assigned to it by that chemist. The author at the same time analysed some salts of Pelosine. According to his analysis, Pel=NH^3 (C^{36} H^{18} O^6):—

Carbon.....	71·94	72·08	36 =	2704·32	72·28
Hydrogen....	7·22	7·04	21	262·08	7·00
Nitrogen	..	..	1	175·06	4·68
Oxygen.....	..	..	6	600·00	16·04

Hydrate of Pelosine, C^{36} H^{21} NO^6, HO+2aq.—Whenever pelosine comes into contact with water or aqueous vapour, it passes into the state of hydrate, which is insoluble in æther. Dried over sulphuric acid, it lost at 248° 8·21 per cent. of water:—

Pelosine	91·79	1 =	3741·46	91·93
Water	8·21	3	337·44	8·27

Muriate of Pelosine, C^{36} H^{21} NO^6, HCl+2HO (dried over sulphuric acid), is obtained when dry muriatic gas is passed into the clear solution of the pelosine dried at 248° in æther, which must be free from alcohol and water, until the solution has an acid reaction; the white flocculent precipitate is quickly collected on a filter, and washed with pure æther until this no longer reddens moist litmus-paper. The filter with the precipitate is then immediately dried over concentrated sulphuric acid. It forms a pure white powder, which is readily soluble in water and alcohol; on evaporating these solutions, it is left behind as a varnish; it quickly absorbs water, and thereby assumes without becoming moist a fused amber-like appearance. The muriate of pelosine lost, by drying at 230°, 4·95 and 5·13 per cent. of water, which with the results of the analysis leads to the formula above given. The salt dried at 230° gave—

Carbon	63·65	63·92	36 =	2704·32	64·44
Hydrogen....	6·58	6·60	22	274·56	6·54
Nitrogen	4·08	..	1	175·06	4·17
Oxygen.....	14·61	..	6	600·00	14·29
Chlorine	11·08	..	1	443·28	10·56

Chloride of Platinum and Pelosine, C^{36} H^{21} NO^6, HCl+$PtCl^2$, obtained by precipitating an alcoholic solution of the pure muriate of pelosine with chloride of platinum, forms a pale yellow, perfectly amorphous and highly electrical powder. After desiccation over sulphuric acid, it lost no more water at 230°. It melts at a higher temperature, puffs up considerably, diffusing an extremely disagreeable odour resembling that of leucoline and carbolic acid. It gave on analysis—

Carbon	43·53	..	36 =	2704·32	42·82
Hydrogen....	4·88	..	22	274·56	4·35
Nitrogen	..	..	1	175·06	2·77
Oxygen.....	..	..	6	600·00	9·50
Platinum	19·13	19·82	1	1232·08	19·50
Chlorine	..	..	3	1329·84	21·06

Chromate of Pelosine, $C^{36}H^{21}NO^6, CrO^3 + 2HO$.—Bichromate of potash produces in a solution of muriate of pelosine a lively yellow precipitate, which in the washing and drying loses its yellow colour and becomes dirty yellowish brown; it grows darker even in the dry state under the air-pump. Heated to 176°, the salt becomes very dark brown; at a little above 212° the whole of the organic matter is rapidly destroyed, with evolution of leucoline and carbolic acid, leaving a mixture of a little carbon with oxide of chromium. This behaviour explains the difference between the calculated and the found results, although the salt employed for the analysis was dried over sulphuric acid:—

Carbon.....	59·07	..	36	= 2704·32	58·85
Hydrogen....	5·55	..	23	287·04	6·24
Nitrogen	..	..	1	175·06	3·81
Oxygen.....	..	..	8	800·00	17·41
Chromic acid	14·52	14·56	3	628·87	13·69

Pelluteine, $NH^3(C^{42}H^{18}O^7)$.—The white pulverulent hydrate of pelosine acquires, under the influence of the air, humidity and light, a deep yellow colour, with disengagement of ammonia. After being boiled with water, in order to convert any unaltered hydrate of pelosine into this new substance, æther no longer dissolved it. The mass is dissolved in boiling absolute alcohol; a humus-like substance is left undissolved, and a light brownish-yellow mass is deposited from the solution in flakes, which were washed with cold alcohol and dried. The name of this substance is derived from *Pelosinum* and *luteum*. It exhibits towards reagents precisely the same behaviour as pelosine, from which it differs by its insolubility in æther and its colour. The substance dried at 230° gave—

Carbon.....	73·99	42	= 3155·04	73·51
Hydrogen	6·18	21	262·08	6·18
Nitrogen	3·84	1	175·06	4·00
Oxygen.....	15·99	7	700·00	16·31

The muriate of pelluteine furnishes with chloride of platinum a double salt, which was found to contain 17·84 per cent. platinum; according to this the atomic weight of pelluteine is 4331·87, and calculated according to the above formula 4292·18.

In conclusion, the author observes, that the bebeerine prepared by Tilley and Maclagan from *Nectandra Rhodiei* possesses many properties in common with pelosine; an essential difference however is apparent in the products of decomposition of the platinum double salts by heat. The chloride of pelosine and platinum disengages an extremely disagreeable odour, resembling that of a mixture of leucoline and carbolic acid, whilst the chloride of bebeerine and platinum diffuses on its decomposition an agreeable odour like that of oil of bitter almonds; it likewise differs in composition, particularly in the amount of water.—Liebig's *Annalen,* lxix. p. 37.

On some Salts of Lithia. By Dr. RAMMELSBERG.

One of the principal objects of the author in undertaking this investigation was to solve the question, whether lithia is capable of forming with sulphuric acid and the earths and metallic oxides double salts like the other alkalies; for hitherto we had only certain information with respect to the combinations of phosphate of lithia with the phosphates of soda and alumina; but as regards the sulphates we merely possessed contradictory assertions. Thus Arfvedson, the discoverer of lithium, thought that he had obtained a combination of sulphate of alumina with sulphate of lithia; but after C. Gmelin's experiments had proved the contrary, he convinced himself that the salt which he had considered to be lithia-alum was nothing more than potash-alum, derived from the potash contained in the alumina employed in preparing the salt. Notwithstanding, Kralowanszky, six years later, again described lithia-alum, and published an analysis, according to which it has exactly the composition of ordinary alum and its crystals the same form. From the description of these experiments, however, it by no means follows that such is the case; for the salt considered in the analysis to be sulphate of lithia was not submitted to any examination. Since the lithia-alum, according to Kralowanszky, is still more insoluble than the potash-alum, inasmuch as it is said to require 24 parts of cold water for solution, it must appear remarkable that this double salt does not crystallize with greater readiness. The author asserts that no such lithia-alum as that described by Kralowanszky exists, and that Arfvedson and C. Gmelin are perfectly right. He modified his experiments in several ways, both as regards concentration, neutrality or acid reaction of the liquid, as also the temperature on evaporation; but never succeeded in obtaining a lithia-alum. Nor could the compound sought for be separated by the addition of alcohol.

The author endeavoured to prepare some new double salts of the sulphate of lithia with other sulphates; and used for that purpose the sulphate of magnesia, oxide of zinc, nickel, cobalt, manganese, protoxide of iron and oxide of copper. Equivalents of the salt of lithia and the sulphate were dissolved, and these solutions crystallized either immediately or after the addition of a little sulphuric acid; in not a single experiment were there any distinct indications of the production of a double salt, but the individual salts constantly crystallized separately. The experience acquired in the course of half a year has led to the result, that no similar double sulphates, such as we are acquainted with in the case of potash, soda and oxide of ammonium, can be obtained with lithia.

The author has also submitted to a more careful examination the chemical relations of lithia, especially its combinations with phosphoric acid. With the exception of the above-mentioned double salt with soda, all our knowledge respecting the combinations of phosphoric acid and lithia is very poor, and entirely of a qualitative nature.

The ordinary (so-called tribasic) phosphoric acid forms with lithia

at least three different salts, viz. that with 3 atoms of lithia, $3LiO, PO^5$; a combination of this and the salt with 2 atoms of lithia and 1 atom of basic water, $3LiO, PO^5 + (2LiO, HO) PO^5$; and lastly, the salt with 1 atom of lithia and 2 atoms of basic water $(LiO, 2HO) PO^5$.

Triphosphate of Lithia, $3LiO, PO^5$, is obtained when phosphate of ammonia and free ammonia are added to an acid solution of the acetate of lithia, or when phosphate of ammonia is added to a neutral solution. It also separates when carbonate of lithia is heated with water and a slight excess of phosphoric acid, in which case the neutral phosphate of lithia remains dissolved. It forms a crystalline powder, dissolves in 833 parts of water at 54°, and does not fuse when heated; it gives with salts of silver a pure yellow precipitate both before and after ignition. It contains 1 atom of water of crystallization, which it parts with on ignition.

The combination of triphosphate and diphosphate of lithia is formed when chloride of lithium is precipitated with phosphate of ammonia. The crystalline precipitate contains no ammonia. It dissolves in 200 parts water; the analyses of it however show that it contains 3 atoms of water, of which two-thirds escape at 212° and five-sixths at 392°; so that half the diphosphate is then already converted into pyrophosphate.

In this salt the acid contains twice as much oxygen as the lithia; however it must not be looked upon as a combination of 5 atoms lithia and 2 atoms phosphoric acid; but must be viewed as a double salt, $3LiO, PO^5 + (2LiO, HO) PO^5 + 2HO$, in which the one member contains 1 atom basic water in the place of 1 atom lithia, although no such separate combination is known. It corresponds however to the ordinary phosphate of soda. A similar double salt exists in the case of lime; it may be prepared artificially by precipitation, and is also contained in bones, $3CaO + 3PO^5$, *i.e.* $2(3CaO, PO^5) + (2CaO, HO) PO^5$, for it must necessarily contain 1 atom of basic water.

The Neutral Phosphate of Lithia, that is to say the salt in which the acid contains five times as much oxygen as the lithia, is obtained,—1st, when the triphosphate is dissolved in a strong acid, the excess expelled, and the residue dissolved and set aside to crystallize; 2nd, when carbonate of lithia is heated with excess of phosphoric acid, and the liquid separated from the triphosphate, evaporated; and 3rd, when a solution of neutral acetate of lithia is evaporated with phosphoric acid. It forms large readily-soluble crystals, which deliquesce in the air; its solution has an acid reaction, precipitates salts of silver yellow, and chloride of barium only upon the addition of ammonia. When heated to 212° it does not decrease in weight, but at a higher temperature water is expelled, and at a red heat it fuses to a clear glass of metaphosphate of lithia, the solution of which immediately produces a precipitate in chloride of barium, and gives a white precipitate with salts of silver. It contains 18 per cent. or 2 atoms of water, half of which it parts with at 392°, being converted into pyrophosphate.—*Berlin Berichte*, Nov. 13, 1848.

On two new Compounds of Phosphoric Acid and Æther. *By* F. Voegeli.

When anhydrous phosphoric acid is made to absorb the vapour of æther under a bell-glass, it is gradually converted into a yellow viscous mass, and becomes perfectly liquid in the course of eight to fifteen days. This liquid, on careful dilution with water and saturation with carbonate of lead, furnishes an insoluble precipitate of phosphate of lead and a sparingly soluble precipitate of æthereo-phosphate (*phosphovinate*), $PO^5, C^4 H^5 O, 2PbO$; while there remains in solution, besides a small quantity of the latter salt, a new salt of lead, $PO^5, 2C^4 H^5 O, PbO$, which the author calls the biæthereo-phosphate of lead. It is easily obtained by evaporating the liquid at a low temperature. At first some laminæ of the æthereo-phosphate separate; after which, on further concentration, groups of needles of the biæthereo-phosphate.

This salt dissolves readily in cold, and still more so in boiling water. It is scarcely soluble in cold absolute alcohol, but readily so at 40°. The crystals thrown upon water exhibit the same gyratory motion as camphor.

At 356° the biæthereo-phosphate of lead fuses, and is decomposed at a little higher temperature, disengaging copious white vapours, which condense into a neutral colourless liquid, miscible with æther, alcohol, and even with water. The residue of the distillation consists of a mixture of phosphate and æthereo-phosphate of lead. The author considers that the distilled product, which boils at 214° and contains phosphoric acid, is the phosphoric æther $PO^5, 3C^4 H^5 O$. He represents the reaction giving rise to this interesting substance in the following manner:—

$$2(PO^5\,2AeO + PbO) = PO^5, AeO, 2PbO + PO^5, 3AeO.$$

The author however states that his experiments and analyses are not yet sufficiently decisive to admit of this phosphoric æther being considered a definite compound.

Anhydrous phosphoric acid likewise furnishes with absolute alcohol æthereo-phosphoric and biæthereo-phosphoric acids. When æther is agitated with syrupy phosphoric acid, combination results as in the preceding cases; but only æthereo-phosphoric acid is formed.

From these experiments it will be seen, that æther, which in the free state possesses the characters of a perfectly neutral body, nevertheless unites directly with certain acids like a base. This important fact, arrived at by Professor Magnus in his investigation of the action of sulphuric acid upon æther, is further confirmed by the experiments of M. Voegeli.—*Journ. de Pharm. et de Chim.*, p. 77.

Experiment to show the Formation of Sulphuric Acid from the Sulphate of the Deutoxide of Nitrogen. *By* Dr. H. Reinsch.

A mixture of 2 parts of sulphur and 3 of nitre is placed upon a piece of tile; this is laid on a flat porcelain plate, which latter is then covered with a large bell-glass, the sides of which have been moist-

ened with water, in such a manner however that the air has access from below; the mixture burns with a brilliant white flame, fills the bell-glass with red vapours, and in a short time the sides of the glass are coated with ice-like acicular crystals of the sulphate of the deutoxide of nitrogen, which on solution in water disengages deutoxide of nitrogen, leaving sulphuric acid in the liquid. This experiment may serve to illustrate the formation of sulphuric acid in the leaden chambers in lectures.—Buchn. *Rept.*, i. p. 367.

Remarks upon Albumen, Caseine and Fibrine. By F. Bopp.

When dilute muriatic acid is added to milk and water in equal volumes until a bulky coagulum and a clear yellowish liquid have separated from each other, which does not occur until the liquid has acquired a strongly acid taste, we obtain a precipitate which differs even in appearance from that produced by acetic acid. It must be separated from the liquid by a linen bag, then diffused through water acidulated with 2 to 3 per cent. of muriatic acid, and again placed upon the bag, and this operation repeated once or twice more. On then washing it with water, in proportion as the acid is washed away the precipitate swells, and in a short time becomes too gelatinous to allow any of the water to pass through. On diffusing the precipitate through a sufficient quantity of water of about 104° F., it dissolves.

This solution still contains a considerable quantity of acid. It is precipitated by acids and alkalies, the latter redissolving the precipitate in excess. But neither of the solutions possess that mucosity which the milk or the solution of ordinary caseine in carbonated alkalies exhibits, and which render it so difficult to separate it from the fat.

On washing the precipitate obtained from the milk by muriatic acid, as stated above, several times with water acidulated with this acid, a slightly turbid solution of caseine is obtained possessing the following properties:—Muriatic acid immediately causes a voluminous precipitate, which does not differ in appearance from that obtained at first. But instead of becoming compact in alcohol, like that obtained from a solution of caseine by acetic acid, it swells in it, and completely dissolves in a sufficient quantity of it. It is precipitable from this solution by æther in white flakes, which swell in water, and subsequently dissolve. Carbonated alkalies produce a precipitate also in the original solution, which is not however soluble in alcohol, but becomes compact; it is soluble in excess. In a recent paper published by Schlossberger, he arrives at the conclusion, that he had separated caseine into two different substances. The above considerations show the origin of his erroneous conclusion. He treated the muriatic solution with a small quantity of carbonate of ammonia, filtered the solution, and added muriatic acid to it, when he obtained another precipitate. As it is scarcely possible to add exactly as much alkaline carbonate as will precipitate the whole of the caseine, somewhat too little or too much will be added. In the

former case the muriatic solution is in excess, in the latter the solution is alkaline; and both yield one and the same precipitate with muriatic acid. Had Schlossberger repeated his experiment several times, he would have found the relative proportions of these two precipitates very variable. On subjecting the two precipitates, one obtained by throwing down the whole of the caseine from the muriatic solution by excess of this acid, and the other prepared by Schlossberger's method, to ultimate analysis, they were shown to be the same. It is evident that caseine forms two compounds with muriatic acid, one of which is insoluble; water however removes part of its acid, and converts it into the soluble compound. The caseine precipitated from the muriatic solution by an alkaline carbonate, may be readily washed with water; and in this way it is easily obtained almost entirely free from fat, without the use of alcohol or æther. The substances considered as different by Schlossberger may be easily converted into each other, by precipitating that existing in an acid solution by an alkali, and that in an alkaline solution with an acid.

The following remarks must be regarded as merely forming the basis of more extensive investigations on the so-called proteine compounds, which the author has not at present time to carry out further.

Action of Caustic Alkalies upon Caseine, Albumen and Fibrine.

It is well known that the most important products of the action of concentrated caustic alkalies upon caseine are leucine and tyrosine. On making a number of preliminary experiments, it was found that there was no striking difference between albumen, fibrine and caseine as regards the action of potash. The great difficulty in obtaining the largest product of leucine and tyrosine consists in arresting the reaction at the proper time, as they are decomposed by the prolonged action of the potash. This object is best attained by abbreviating the duration of the reaction as much as possible, regardless of its intensity. For this purpose, equal parts of dry hydrate of potash and the dried substance are taken; the former fused in its water of crystallization in an iron vessel, and the finely pulverized substance projected into it, replacing the water lost in small quantities at a time. Violent effervescence takes place from the evolution of ammonia and hydrogen, and a peculiar odour accompanies these gases. The only certain criterion of the completion of the process is the alteration in colour. The dark brown colour which is seen at first must just pass into yellow if tyrosine is required as well as leucine. This tint can only be recognized by practice. The mixture should be stirred with an iron spatula, and the operation must not continue more than half an hour. When the peculiar colour appears, it must be interrupted by the careful addition of water, then saturated with acetic acid, filtered and allowed to cool. If the operation is successful, groups of concentric needles of tyrosine fill the entire fluid. The liquid is then evaporated until a pellicle is formed on the surface, set aside for twenty-four hours, and

treated with strong alcohol, which leaves a residue usually consisting of small granules made up of concentric plates and needles. This is leucine, with perhaps an admixture of tyrosine. Sulphuric acid diluted with alcohol is added to the alcoholic solution as long as sulphate of potash separates. The alcohol is expelled, the sulphuric acid remaining in the solution precipitated by acetate of lead, and the excess of lead removed by sulphuretted hydrogen. The liquid is then evaporated, when a fresh quantity of leucine separates. The tyrosine thus obtained is separated from the leucine by recrystallization from water and subsequent washing with a little cold water, in which it is but little soluble, although it is far more so in hot water. It is then purified from a brownish-red matter which accompanies it, by dissolving it in a little muriatic acid and treating it with animal charcoal, adding as much acetate of potash as corresponds to the muriatic acid used, and rapidly filtering; it then separates in a fine network of needles, which fill the whole fluid. The acetic acid retains in solution a small quantity of ash, which adheres tenaciously to the tyrosine when crystallizing from a neutral solution. When purified by recrystallization from water, it possesses a brilliant pearly lustre.

The leucine is separated from the last portions of tyrosine by solution in so much hot water that a small quantity only of the leucine, and with it the tyrosine, crystallize out; the very minute quantity of tyrosine which still remains in the liquid, is precipitated by basic acetate of lead, or what is better a little hydrated oxide of lead, with the colouring matter and a little leucine, although a pure solution of leucine and tyrosine is not precipitated by basic acetate of lead. The lead is separated by sulphuretted hydrogen, the sulphuret appearing to exert a decolorizing action; a still yellowish liquid is then obtained, which on evaporation in a retort until a pellicle forms solidifies to a mass of leucine, which is then washed on a filter with cold water, and subsequently with alcohol, and purified by recrystallization and treatment with animal charcoal.

If the process be interrupted immediately after the first powerful effervescence has ceased, the product consists of leucine only.

The action of muriatic acid upon leucine and tyrosine, which dissolves but does not decompose them, and also of dilute sulphuric acid, with which acids they may be evaporated at a temperature not exceeding 212°, induced me to investigate the

Action of Muriatic and Sulphuric Acids upon Caseine, Albumen and Fibrine.

Braconnot, as is well known, stated that on treating muscle, gelatine, wool and legumine (vegetable caseine) with sulphuric acid, leucine is obtained; whilst Mulder states that on subjecting albumen to the action of muriatic acid, it is resolved into muriate and humate of ammonia only. The author found Mulder's statement incorrect; for on boiling albumen, or either of the other substances, with from four to five times its amount of concentrated muriatic acid for six or eight hours, the whole product of leucine and tyro-

sine obtainable is procured. This equally occurs whether access of air is permitted or not. The mass which Mulder considers to consist of the ammonia-salt of the acid used and humate of ammonia, is dissolved in hot water, milk of lime added to it, the mixture boiled for some time to remove the ammonia, and filtered as quickly as possible through a linen bag. The lime dissolved in the liquid is precipitated with a little sulphuric acid, the excess of this by acetate of lead, and the lead by sulphuretted hydrogen. On evaporation, a syrupy mass is obtained; this is set aside for several days, and the leucine and tyrosine which have subsided in crystals are separated from the syrup by alcohol of 0·845 sp. gr., in which the latter dissolves. The two crystalline matters are separated and purified as above, by their different solubilities in water, &c.

In the syrupy liquid remaining after the separation of most of the leucine and tyrosine (a mixture of muriatic and sulphuric acids having been substituted for the former alone), after having been set aside for about two months, a large number of groups of crystals were found; and by rapidly triturating them with cold water, they were separated from the remaining mass. They consisted principally of leucine, but contained also some crystals of a new crystalline substance distinct in its properties from either leucine or tyrosine. This is readily shown by the following comparison:—

1. *Leucine* sublimes without residue, forming woolly flakes; is readily soluble in water; difficultly soluble in absolute alcohol; readily soluble in muriatic acid and potash; forms pearly scales, which are frequently grouped concentrically.

2. *Tyrosine* cannot be sublimed, but when heated is decomposed, evolving an odour of burnt horn; difficultly soluble in water; almost insoluble in alcohol; readily soluble in muriatic acid and potash; forms pearly crystals, frequently grouped concentrically, and remarkable from their extraordinary volume when crystallized from water.

3. *New Crystalline Substance* sublimes in woolly flakes without residue; difficultly soluble in water; readily soluble in absolute alcohol; almost insoluble in muriatic acid and potash; forms needles, without any particular lustre, which when crystallized in small quantity from absolute alcohol, are as remarkable from their extraordinary size as tyrosine when deposited from water.

This substance was obtained from fibrine, albumen and caseine. Its quantity was not sufficient for further examination.

Products of the putrefactive Decomposition of Albumen, Fibrine and Caseine.—A mixture of either of these substances with forty or fifty times as much water, when exposed at a temperature of about 70° F. to the atmosphere, enters into putrefaction, the solid body disappearing; and in from four to six weeks the properties of the substance used are no longer recognizable, in consequence of its having been completely decomposed. It is worthy of remark regarding fibrine, which in other respects undergoes the same changes as caseine and albumen, that in a few days it dissolves, and the solution is coagulable by heat, like a solution of albumen. On the further examination of the pu-

trefied liquids obtained with fibrine, caseine and albumen, the author detected ammonia, leucine, tyrosine, valerianic and butyric acids, and a substance resembling benzoic acid; but as the exact nature of the substances has not been satisfactorily ascertained, we shall omit the further details of his experiments.—*Ann. der Pharm. und Chem.*, vol. lxix. p. 16.

Note on the Crystallized Phosphate of Lime.
By J. Percy, M.D., F.R.S.*

In the third volume of the 'Chemical Gazette,' p. 86, is a notice of a crystallized hydrate of phosphate of lime, which I prepared by passing carbonic acid through water containing suspended in it phosphate of lime obtained by mixing dilute solutions of chloride of calcium and common phosphate of soda. I analysed the crystallized phosphate so produced, and assigned to it the following composition, $2CaO, PO^5, 6HO$. On looking over the details of my analyses, I find that, in deducing the formula, I have committed an error of 1 equiv. of water. In composition this phosphate is identical with that of the animal calculus analysed by Wöhler (Berzelius, Rap. An., 1846, p. 530) and that of Dr. Bödeker, noticed in the last number of the 'Gazette.' Berzelius remarked, that as my analysis was only made upon $3\frac{1}{4}$ grs., it was uncertain whether my determination of the proportion of water was correct. However, the following result will show that my error consisted not in the details of the analyses, notwithstanding the smallness of the quantity operated upon, but, as I have remarked, in deducing the formula:—

	Analyses by J. P., Rep. Chem. Soc. I.	II.
Water	0·85	0·84
Lime	1·04	1·02
Phosphoric acid	1·32	1·30
	3·21	3·16

	Calculated per cent. I.	II.
Water	26·47	26·58
Lime	32·39	32·27
Phosphoric acid	41·12	41·13
	99·98	99·98

	Mean of the two.	Dr. Bödeker's analysis.
Water	26·52	26·22
Lime	32·33	32·56
Phosphoric acid	41·12	41·22
	99·97	100·00

* Communicated by the Author.

The ratio of the oxygen from my analyses is—

		Oxygen.
Water	23·57	5·2
Lime	9·09	2·0
Phosphoric acid	23·04	5·1

whence evidently the rational formula will be $2CaO,HO,PO^5+4HO$.

The excess of water which appears in my analysis is evidently due to imperfect desiccation, as I did not, like Dr. Bödeker, dry the specimen which I analysed over chloride of calcium.

The physical characters of the phosphate of Dr. Bödeker are exactly the same as those of the phosphate described by myself.

On a future occasion I may communicate to the 'Gazette' additional results concerning the phosphate, which I obtained several years ago, and which relate especially to the deposition of phosphate of lime by heat from urine under particular circumstances.

I have prepared a very beautifully crystallized phosphate of magnesia by the same process as that by which I procured the crystallized phosphate of lime; but I have not yet subjected it to analysis. It appears to contain a very large quantity of water, as it rapidly effloresces and becomes opake when exposed to warm air.

Examination of the expressed Oils of Black and White Mustard Seed. By S. Darby.

The fat oil expressed from *white* mustard seed furnishes with soda a soap, which is entirely soluble in water, and glycerine. The soap was separated with chloride of sodium and decomposed with muriatic acid; the liquid mixture of fatty acids was converted by digestion with oxide of lead into basic lead compounds. The lead soap was treated with æther, which dissolved a portion, leaving another undissolved; the latter contained an acid, which the author calls *erucic acid*. The acid in the lead compound soluble in æther is perhaps distinct from oleic acid; but this the author leaves undecided.

Erucic Acid, $C^{44}H^{41}O^3,HO$, is obtained from the above insoluble lead compound by decomposing it with muriatic acid and alcohol, separating the chloride of lead and distilling off the alcohol; the residual acid is washed with warm water, frequently crystallized from alcohol until it appears perfectly white and has a constant melting-point. It separates from the alcoholic solution in shining acicular crystals, melts at 93°, and solidifies at 91°. It is most closely allied in its constitution to the behenic acid, $C^{44}H^{44}O^4$, examined by Völker, if we admit the corrected formula adopted by Strecker. The perfectly dry acid gave on analysis—

Carbon	77·8	77·5	77·3	44 =	264	78·1
Hydrogen	12·5	12·9	12·4	42	42	12·4
Oxygen	9·8	9·7	10·3	4	32	9·5

Erucate of Silver, $C^{44}H^{41}O^3$, AgO, obtained by precipitating with nitrate of silver an alcoholic solution of erucic acid supersaturated with ammonia, forms a caseous precipitate, which soon acquires a dark colour, and which, immediately after washing and pressing between blotting-paper, must be dried *in vacuo* over sulphuric acid. It gave on analysis—

Erucic acid	..	..	1 =	329	74·0
Oxide of silver	26·0	25·7	1	116	26·0

Erucate of Lead, $C^{44}H^{41}O^3$, PbO.—The solution of erucic acid in absolute alcohol neutralized with carbonate of soda furnishes with an alcoholic solution of acetate of lead a white precipitate, which, after being washed with alcohol and dried *in vacuo*, gave on analysis—

Carbon	59·7	..	44 =	264	59·9
Hydrogen	9·3	..	41	41	9·3
Oxygen	..	..	3	24	
Oxide of lead	25·28	25·5	1	112	25·26

Erucate of Baryta, $C^{44}H^{41}O^3$, BaO.—An alcoholic solution of erucate of soda furnishes with an alcoholic solution of acetate of baryta a white flocculent precipitate. Dried *in vacuo* and analysed, it gave—

Carbon	64·36	44 =	264·0	65·0
Hydrogen	10·40	41	41·0	10·1
Oxygen	..	3	24·0	
Baryta	18·90	1	76·6	18·8

The lead salt described above as soluble in æther was mixed with alcohol and muriatic acid, and after evaporating the æther, the chloride of lead separated by filtration, the alcohol removed by distillation, and the residual fatty acid converted, according to the method described by Gottlieb, into a baryta salt. The analysis of this baryta salt does not agree with the composition of the oleate of baryta; for the latter, $C^{36}H^{33}O^3$, BaO, contains 61·79 C, 9·4 H, and 21·9 BaO, whilst the analysis of this acid gave the following results, which correspond most closely to the formula $C^{38}H^{36}O^4$, BaO:—

Carbon	60·57	61·20	38 =	228·0	61·2
Hydrogen	9·81	9·76	36	36·0	9·6
Oxygen	..	..	4	32·0	8·8
Baryta	19·99	20·00	1	76·6	20·4

The fat oil from black mustard seed contains stearic acid, erucic acid, and apparently the acid last described. The lead soap obtained after saponification, &c. is separated as above by æther into an insoluble and a soluble portion; the insoluble portion then contains stearic and erucic acids, which are separated by crystallization. The first portions which separated had, after frequent recrystallization, a melting-point situated a little above 158°, and, as the analysis of the baryta salt prepared with this acid proves, is stearic acid:—

Carbon	60·68	60·95	68 =	408·0	61·08
Hydrogen.....	10·10	10·50	66	66·0	9·90
Oxygen.....	..	..	5	40·0	
Baryta	22·99	..	2	153·2	22·96

The alcoholic mother-ley from which the stearic acid had separated contained an acid having all the properties of erucic acid. Its baryta salt furnished 19·0 per cent. baryta, and it melted at 93°.—Liebig's *Annalen*, lxix. p. 1.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

Process of extracting Nickel and Cobalt followed in a Manufactory at Birmingham. By M. Louyet.

The ore employed in this manufactory is obtained from Hungary. It consists principally of metallic sulphoarseniurets, and contains generally 6 per cent. of nickel and 3 per cent. of cobalt. These proportions however vary.

The ore is mixed with a small quantity of carbonate of lime and fluor spar, and the whole heated to a white-red in a reverberatory furnace; the mass fuses at this high temperature, and a slag is obtained floating on the surface, which is removed, and a fluid mass of metallic appearance; the latter is let out of the furnace by a particular aperture, and watered in order that it may be broken into fragments with greater facility. It has been ascertained from experience that when the slag is of a dull colour, it contains iron; but if its surface is black and brilliant, it is free from it. The metallic mass is reduced to a very fine powder, which is then calcined at a bright red in a furnace, graduating the temperature so as to avoid fusion, and constantly raking it: a considerable quantity of arsenious acid is driven off. The air has free access to the mass, which becomes oxidized and diminished in weight. The calcination, which lasts for about twelve hours, is continued until no more white fumes are given off, and the residue is treated with hydrochloric acid, which dissolves nearly the whole of it; the liquid is diluted with water, and milk of lime and hypochlorite of lime (chloride of lime) added*, when a precipitate falls, which after being well washed is thrown away. A current of washed sulphuretted hydrogen, generated from sulphuret of iron and dilute sulphuric acid, is passed into the liquid until it is saturated; it is discontinued when some ammonia, added to a sample of the filtered liquid, gives a black precipitate; if there was not an excess of sulphuretted hydrogen, the precipitate produced by ammonia would be green. The sulphuretted hydrogen causes a

* The lime and hypochlorite of lime are added to precipitate the iron and arsenic; the hypochlorite, by peroxidizing the iron, admits of its being precipitated by the lime.

precipitate in the liquid; it is washed, and as it is slightly soluble, a current of sulphuretted hydrogen is passed into the wash-waters. The precipitate is thrown away. The cobalt is then thrown down with a solution of hypochlorite of lime. The precipitate, washed, dried, and then heated to redness, is considered to be oxide of cobalt, and part is sent in this state into the market; another portion is heated to a white-red; by this treatment the oxide loses in weight, but increases in density; it is sold as protoxide of cobalt. The liquid from which the cobalt has been precipitated is treated with milk of lime, which precipitates the nickel in the state of hydrate; this precipitate is washed, dried and heated to redness; it is then mixed with charcoal, and by means of a strong heat reduced to the state of a spongy nickel, which is employed in the manufacture of German silver. With respect to the oxide of cobalt, nearly the whole of it is consumed in the Staffordshire potteries. The oxide of cobalt thus prepared is remarkably pure.—*Bullet. de l'Acad. Royale de Belgique.*

Examination of some kinds of Chinese Copper. By H. Onnen.

Of the following analyses, those of the red coppers show an amount of nickel and cobalt; tin, which is usually found in coins and commercial copper, was not met with in Chinese copper. Nos. II. and IX. contain a considerable quantity of iron, while in the white copper there is a small quantity of silver. The yellow kinds are alloys of zinc and copper, and the white either of copper and nickel, or copper, nickel and iron. The presence of sulphur deserves attention. The kinds analysed are characterized as follows:—

I. Chinese copper or packfong, consisting of a broad plate. It was exteriorly and upon the fracture of a whitish-yellow colour.

II. White copper or packfong; a ring, the colour of which was blackish externally and the fracture irregularly yellow.

III. A sample consisting of several irregular thin pieces, which had been broken off a cake of copper, of a beautiful red colour externally and on the fracture.

IV. Chinese copper, best kind, a semicircular smooth piece, externally and on the fracture of a beautiful red colour.

V. Chinese copper, second kind, a smooth semicircular piece, externally and on the fracture of a copper-red colour.

VI. Chinese copper, third sort, resembling the piece No. V.

VII. Chinese copper, best kind, a thin plate broken off a round piece, externally and on the fracture of a copper-red colour.

VIII. Chinese copper, second kind, a thick square piece, with granular fracture, and coloured blackish-red by the presence of oxide.

IX. resembled No. VIII.

The specific gravity of these samples of copper was—

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
8·57	7·84	8·31	8·93	8·70	8·45	8·58	8·70	8·46

The analyses gave the following composition:—

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
Silver ..	0·12	0·44	0·14	0·505	0·07	0·07	..	..	..
Copper ..	87·54	85·09	98·49	97·790	82·21	62·49	97·12	92·65	93·48
Iron	1·17	4·08	0·01	0·210	0·19	0·40	1·28	0·10	4·43
Nickel ..	11·48	9·49	1·19	1·350	0·71	0·74	1·84	2·11	0·46
Cobalt ..	0·44	1·16							
Sulphur	0·10	0·49	..	..	..	..	0·30	0·06	0·47
Zinc	..	..	..	..	17·56	35·84			
Lead	..	..	..	..	..	..	..	5·75	

Journ. für Prakt. Chem., vol. xliv. p. 242.

PATENT.

Patent granted to Alexander Angus Croll, Tottenham, Middlesex, *for Improvements in the Manufacture of Gas.*

The first part of this invention relates to the manufacture of gas by the use of retorts which can be fed at each end.

When such retorts have been heretofore used, they have been provided with a rising pipe at each end to carry off the gas produced, instead of which the patentee applies a rising pipe only at one end of the retort; and in place of feeding both ends alternately and at distant periods one from the other, he charges both ends at the same time. He states that considerable advantages will result from this improvement.

The second part of this invention consists in passing steam through carbon at a bright red heat, and then causing it to pass over or amongst the charge of coal which is being distilled in a retort.

The patentee prefers to use retorts such as those above described. He charges the same with coke at the end most distant from the rising pipe, to which end he also applies a pipe for introducing steam; and at the other end of the retort he introduces a charge of coal once in every five hours, allowing the steam to flow in for about three hours after the introduction of such charge. He has found that advantageous results may be obtained by evaporating 15 lbs. of water, and passing the steam into the retort, for each ton of coals distilled (that is to say when Newcastle coal is used, but when Kennet coal is used the quantity should be increased); he does not however confine himself to this proportion, the object being to obtain a larger quantity of gas of a fair illuminating power and a smaller quantity of tar.

The third part of this invention consists in the employment of sulphurous acid in such manner as to deprive carburetted hydrogen gas of the sulphuretted hydrogen gas with which it is contaminated, and thus to obtain the sulphur of both compounds in the form of flowers of sulphur.

A solution of sulphurous acid in water is made by connecting a vessel or vessels of cast iron (arranged as a Woolfe's apparatus) with an oven in which sulphur is burned, and by means of an air-pump causing a current of sulphurous acid gas from the burning sulphur to pass through the water contained in the vessel or vessels until the same is nearly saturated with sulphurous acid; to effect this, about 6 oz. of sulphur must be burned for each gallon of water. The solution is transferred to the first of three vessels, which are constructed and arranged in the same manner as the ordinary wet-lime purifiers; and the other two vessels are charged with a weaker solution, derived, after the process has been once performed, from the washers hereafter mentioned, and from a portion of the sulphurous acid which is disengaged from the first vessel. The gas is passed through the three vessels in succession, commencing with the first, whereby the sulphuretted hydrogen in the coal gas and the sulphurous acid are both decomposed, and sulphur is deposited. When the sulphurous acid in the first vessel has been all decomposed, or nearly so, the contents are discharged into a suitable receiver, in which the sulphur may settle, or it may be separated from the liquor by filtration; and it is to be afterwards dried. The first vessel is charged with a fresh solution, and the operation goes on as before.

Instead of preparing the solution of sulphurous acid in a separate vessel, and using one set of purifiers, as above described, the patentee prefers to employ two sets of purifiers alternately, and to charge the liquid with sulphurous acid in the first vessel of one set while the coal gas is passing through the other set; and instead of using water to form the solution, he prefers to transfer the liquid, already partially charged, from the second vessel into the first, to supply the second vessel from the third, and to change the third from the washers.

Owing to the volatility of the sulphurous acid, a portion of it is carried over with the gas; and therefore, to free the gas from this impurity, it is caused to pass through three other vessels, called washers; and finally, to remove every trace of impurity, it is passed through a common dry lime purifier. The washers are arranged so as to be put in connexion with either series of purifiers at pleasure; and any construction may be adopted which will admit of the gas passing freely, and at the same time being thoroughly exposed to the water: the ordinary lime purifiers answer well for this purpose. The washers are charged with water only; and as it becomes impure it is transferred through the series onward, and then into the purifiers—only the last vessel of the series being supplied with the fresh water.

The last part of this invention relates to the mode of transmitting gas through mains to supply districts at a distance from the gas-works.—Sealed August 22, 1848.

THE CHEMICAL GAZETTE.

No. CLVII.—May 1, 1849.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Composition of Stearic Acid.
By MM. LAURENT *and* GERHARDT.

ACCORDING to the most recent analyses which have been made in Germany by the process generally in use, and under the direction of M. Liebig, the composition of stearic and margaric acids came to the support of the theory of organic radicals, by assigning to these acids formulæ similar to those of hyposulphuric and sulphuric acids. In a word, these two acids, supposed in the anhydrous state, presented two different stages of oxidation of the same radical, R^2O^5 and RO^3, R expressing the composition of a hypothetical radical, margaryle, $C^{34}H^{66}$*.

On taking into consideration the great analogy of the physical characters of these two acids and the perfect identity of their chemical properties, that is to say of their metamorphoses under the influence of reagents, we were led to doubt the accuracy of the formulæ which established between them so great a difference. On the other hand, the formula attributed to stearic acid was in contradiction to the propositions we have advanced respecting the divisibility of the formulæ of organic substances. Either these propositions were false or the composition of stearic acid adopted by the Giessen school was inaccurate. Experiment could alone decide this. Now we have found, in the first place, that stearic and margaric acids have the same atomic weight; on this point we agree with all those chemists who have analysed the salts. We have made seven analyses of stearic acid, derived from four different sources. The differences between the analyses amount for the carbon to one or two-thousandths, and scarcely to one-thousandth for the hydrogen. They lead exactly to the formula of margaric acid, viz. $C^{34}H^{68}O^3$. We have likewise observed, as was announced by M. Chevreul long since, that pure stearic acid may be distilled for the greater part without alteration, and that it behaves in this respect like all the other volatile acids of the same homologous series, as formic, acetic, butyric acids, &c. If, under certain circumstances, this distillation is accompanied by the formation of other products, for instance

* Margaric acid, $C^{34}H^{66}O^3+H^2O$; stearic acid, $2(C^{34}H^{66})O^5+2H^2O$ (bibasic) $=C^{68}H^{136}O^7$, with the oxygen indivisible by 2.

liquid hydrocarbons, they may be entirely avoided by distilling from 15 to 20 grms. of the pure acid, and interrupting the operation as soon as the last portions acquire a faint brownish tint. Again, if some German chemists have observed in the distilled acid a lower melting-point, which led them to view the product as margaric acid; this decomposition, if it occurs, is effected, according to us, without any decomposition, and can only be the result of some molecular change.

In fact, a greater difference does not exist between stearic and margaric acid than between tartaric and metatartaric acid; they are two physical varieties of one and the same chemical species; margaric acid should be called metastearic acid.

This result is moreover confirmed by all the reactions known of these bodies; the identity of composition and of characters of the substances described by M. Bussy under the names of margarone and stearone; the identity of the results obtained by M. Erdmann in the analyses of the products of anhydrous phosphoric acid upon stearic and margaric acids; lastly, the identity of the atomic weights of these two acids—all these facts now find their natural explanation in this state of isomerism which we have pointed out.

The chemical history of the fatty substances is thus simplified. Physiology will be interested in the result, for it does away with that inexplicable and most singular difference which seemed to exist between the composition of the fatty bodies of man and the pig and that of other animal fats.—*Comptes Rendus*, March 26, 1849.

On the Analysis of the Ashes of Organic Substances.
By M. Fleitmann.

Every one occupied with the analysis of ashes knows the difficulties which accompany the incineration of many substances. The escape of alkaline chlorides during the process is known to be great. Other salts are driven off or altered, especially the phosphates, which are reduced by charcoal at the high temperature necessary for combustion. Starting with the supposition that the principal cause of the difficulty of burning the charred masses arises from the envelope of fusible salts, which exclude the free access of air, I tried to improve the process by obstructing that influence. I succeeded in this by charring the substance, powdering, moistening with bichloride of platinum, and igniting the whole in the open air. In this manner the entire substance became penetrated with a fine net-work of platinum sponge. The well-known property of platinum sponge, of absorbing oxygen in its pores and transferring it to combustible bodies, is here of great avail. This property shows itself in so striking a manner, that frequently the charcoal prepared with platinum as indicated, when once lighted, continues in a state of ignition for hours without the application of external heat. The maximum quantity of platinum is $\frac{1}{2}$ a grm. for 10 grms. of charred substance. The separation of the platinum from the ashes is simple; one difficulty has to be overcome. In most cases where the charred substance

is incorporated with the solution of chloride of platinum, a quantity of double salts of platinum is formed, which cannot be perfectly decomposed by simple ignition. A reduction by means of hydrogen is therefore unavoidable.

The determination of the chlorine contained in the ashes is of course to be made beforehand. The substance is to be charred in a well-closed Hessian crucible, then completely extracted with water, and the chlorine determined from that solution. In my analyses I used to analyse this solution by itself. I then proceeded to extract with hydrochloric acid, and analysed this solution separately and also the residue. I did this at the request of Prof. Rose, who has founded on these results a theory which he will soon publish.

I give below the result of my analysis of the fæces and urine of man, which I have tried to make interesting by enabling a comparison to be made between the inorganic matters they contain and those contained in the food at the same time.

I carefully collected for four days the solid and liquid excrements of a young man. The sum of the constituents in both can without doubt be regarded as equivalent to the corresponding quantities in the food. The following quantities are calculated for the period of twenty-four hours:—

	The fæces of one day contain		The urine of one day contains	
NaCl.....	=0·0167	gramme.	=8·9243	grammes.
NaO.....	0·0185	...		
KCl	..		0·7511	...
KO	0·5455	...	2·4823	...
CaO	0·5566	...	0·2245	...
MgO.....	0·2781	...	0·2415	...
Fe^2O^3	0·0544	...	0·0048	...
PO^5	0·8072	...	1·7598	...
SO^3	0·0293	...	0·3864	...
SiO^3	0·0375	...	0·0691	...
	2·3438		14·8438	

The difference in the proportions of potash and soda in the fæces and urine is remarkable. The quantity of soda in the fæces is in no proportion to that which is secreted daily in the body as bile, and shows that the bile must be removed from the body by some other way than the fæces.—Silliman's *Journal*, March 1849.

On a new kind of Copaiva Balsam. *By* Dr. L. Posselt.

The various kinds of copaiva balsam hitherto met with in commerce furnish, when mixed with a solution of potash or ammonia, a more or less clear solution. After some time the ammoniacal solution deposits the ammonia salt of an acid resin, the copaivic acid. When this reaction does not take place, it has hitherto generally been assumed that the balsam has been adulterated. The author procured from England a balsam which had been derived from

South America, the genuineness of which was guaranteed, and was likewise placed beyond all doubt by the results of analysis; he is therefore of opinion that there exists a distinct kind of copaiva balsam, which has the greatest resemblance to the ordinary kind, but differs considerably from it in its characters. It is more liquid and of a lighter yellow colour, has the peculiar disagreeable odour of the ordinary balsam, and also the lasting taste. Its specific gravity is 0·94. Mixed in any proportion with solution of potash or ammonia, it remains turbid, and never forms with it a soapy mixture, but after a time again separates from those liquids. It does not dissolve perfectly in alcohol, but forms a milky liquid. It contains 82 per cent. of oil and 18 per cent. of resin, which latter is partly soluble and partly insoluble. The oil in the pure state is a

Hydrocarbon, $C^{10} H^8$, which the author calls *paracopaiva oil*. It is obtained by distilling this copaiva balsam with water. After a second distillation with water, the hydrocarbon forms a colourless thick oil, of a strong pure odour of copaiva and an acrid burning taste; spec. grav., 0·91; boiling-point, 485°. This however quickly and uninterruptedly rises, the boiling oil being decomposed. It becomes yellowish, thickish, then brown, thick and tenacious, until it is finally decomposed entirely with separation of carbon. It mixes in every proportion with æther, requires a rather large quantity of absolute alcohol for solution, and dissolves with great difficulty in spirit of 0·863 spec. grav. Dry muriatic gas combines with it, forming a brown liquid with a reddish tint, which when saturated fumes in the air. No crystalline compound could be separated from it. This paracopaiva oil differs therefore from the ordinary oil by its thickness, its behaviour towards alcohol, muriatic acid gas, and its boiling-point.

Nitric acid of 1·32 spec. grav. has no action upon the oil at the ordinary temperature; but on the application of heat, it is converted, with a violent reaction, into a resinous substance. It dissolves entirely in dilute nitric acid in some days, when nitrous acid, carbonic acid, and some peculiar volatile acids which furnish a precipitate with basic acetate of lead, escape. The residue, evaporated and diluted with water, deposits an acid resin, which is not further acted upon by nitric acid, whilst a crystalline acid remains dissolved in the liquid.

The resin is of a light yellow colour, somewhat soluble in boiling water; it becomes milky on cooling. It dissolves readily in æther and alcohol, and after a considerable length of time some small crystals of the resin are deposited. It has an acid reaction, and combines with potash and ammonia, forming red neutral compounds soluble in water.

The acid left in solution crystallizes in minute, colourless, transparent laminæ. It is readily soluble in water, alcohol, æther and naphtha. It is free from smell, has a bitter taste and a faint acid reaction. It deflagrates with fuming nitric acid. Iodine dissolves in it; with chlorine it gives off vapours of muriatic acid gas, and then becomes yellow and tenacious. It acquires a dark violet-red

colour when treated with concentrated sulphuric acid. The analysis of the paracopaiva oil gave—

Carbon	88·13	10 =	60	88·23
Hydrogen	11·77	8	8	11·77

The resin, which with the paracopaiva oil constitutes the original balsam, was prepared by boiling the residue of the distillation of the oil with water to expel the remainder of the oil. The residual pale brown friable mass consists of two different resins, one of which is readily soluble and the other insoluble in alcohol. The *soluble* resin forms the greater portion of the mixture, and may be readily obtained pure by repeated solution in alcohol, when the second resin is left behind. It is light yellow, easily reduced to powder, soft at a gentle heat, and is decomposed at a slightly elevated temperature, becoming dark-coloured and forming a thick liquid. It dissolves in weak boiling spirit, but separates for the greater part on cooling in white flakes; it is likewise readily soluble in strong alcohol in the cold, in æther and in naphtha. The alcoholic solution does not possess an acid reaction; no precipitate is produced with acetate of copper; it is insoluble in potash or ammonia. On analysis this resin was found to contain 60·06–59·98 per cent. carbon and 8·48–8·27 hydrogen.

The resin *insoluble* in alcohol is repeatedly exhausted with absolute alcohol, dissolved in æther and separated by evaporation; it has the same colour as the preceding one, is insoluble in dilute alcohol, and very sparingly soluble in boiling absolute alcohol, from which solution it mostly separates on cooling; it dissolves readily in æther and naphtha; the solution is not acid. It is perfectly insoluble in potash or ammonia. On boiling these liquids with the resin, they become opake, and deposit on cooling the suspended resin. The solution of the resin furnishes with acetate of copper a slight precipitate. On analysis the resin furnished 81·76–82·12 carbon and 10·56–10·48 hydrogen.

It results from this investigation that this balsam is not ordinary copaiva balsam adulterated, but a distinct kind. The author had no opportunity of making any experiments as to its effectiveness.—Liebig's *Annalen*, lxix. p. 67.

Experiments on the Nitrogenous Compounds of the Benzoic Series. *By* G. Chancel.

These experiments relate principally to the action of the hydrosulphate of ammonia upon nitrobenzamide. This substance was first obtained by Mr. Field by the action of heat upon the nitrobenzoate of ammonia; but this process does not always succeed, and I have found it most advantageous to prepare it from nitrobenzoic æther and ammonia.

The action of the hydrosulphate of ammonia upon nitrobenzamide dissolved in alcohol is frequently very complex, whilst with an aqueous solution it is very simple; in the latter case there is a con-

siderable deposit of sulphur and of crystals, which according to my analyses contain $C^7 H^8 N^2 O$ + aq. The water of crystallization is expelled between 212° and 248°.

The formation of this body is in conformity with the known reactions of the hydrosulphate of ammonia upon nitrogenized substances; we have, in fact, $C^7 H^6 XNO + 3SH^2 = C^7 H^8 N^2 O + 2OH^2 + 3S$*; but if the formation of this substance comes within the known reactions, the change of functions which has taken place is hitherto without example in organic chemistry; for it no longer belongs to the benzoic series, but represents carbanilamide or anilamic urea, that is to say a double carbonate of aniline and ammonia less 2 equivs. water $(CH^2 O^3, C^6 H^7 N, NH^3) - 2OH^2 = C^7 H^8 N^2 O$. This opinion is founded upon the following facts:—When carbanilamide is heated with potash-lime, ammonia is disengaged at a slightly elevated temperature, which I determined in the state of the platinochloride. When heated still more strongly, no more ammonia is given off, but only pure aniline. The following equation will explain this metamorphosis:—

$$C^7 H^8 NO + 2OKH = CO^3 K^2 + C^6 H^7 N + NH^3.$$

But this equation evidently does not represent the final reaction, and we must distinguish two phases, in

The first, $C^7 H^8 NO + OKH = NH^3 + C^7 H^6 KNO^2$.
The second, $C^7 H^6 KNO^2 + OKH = C^6 H^7 NCO^3 K^2$.

The salt of potash which is produced in the first phase must be the anthranilate or an isomeric compound, in all cases the true carbanilate.

This experiment proves that carbanilamide contains the constituents of 1 equiv. ammonia and of 1 equiv. aniline. The action of sulphuric acid is equally distinct, and supports my opinion; it furnishes, in fact, sulphanilic acid and sulphate of ammonia, with disengagement of carbonic gas:—

$$C^7 H^8 NO + 2SO^4 H^2 = CO^2 + C^6 H^7 NSO^5 + SO^4 H^2, NH^3.$$

By acting with cyanic acid upon aniline, M. Hofmann obtained a substance to which he likewise assigns the composition of anilamic urea. As this chemist has merely announced the production of this substance without describing its properties, I am not able to assert their identity.

Carbanilamide possesses the following properties:—It is soluble in water, alcohol and æther; its alcoholic or æthereal solution quickly acquires a dark red colour, and appears to experience some change, but its aqueous solution is not altered, and furnishes on spontaneous evaporation very beautiful, transparent, flattened prisms of considerable size. The crystals have no odour; they have a cool, very slightly bitter taste, similar to nitre; they contain 1 equiv. water of crystallization, melt at 161°, and are decomposed at a higher temperature, leaving a large amount of carbon.

* $X = NO^2$ C = 12 H = 1 O = 16 N = 14, notation of M. Gerhardt.

Carbanilamide, like urea, combines with acids and metallic salts, furnishing crystalline compounds. I have analysed the following:—

The nitrate ..... $C^7 H^8 N^2 O, NO^3 H$
The argentonitrate ..... $C^7 H^8 N^2 O, NO^3 Ag$
The chloride..... $C^7 H^8 N^2 O, ClH$

I likewise obtained the hydrargyrochloride and the platinochloride.

In concluding this extract, I may state that I have also analysed the æthers of nitrobenzoic acid; that from alcohol crystallizes in right rhombic prisms of 122°; my analyses confirm those of M. Kopp; that from pyroligneous æther crystallizes in nearly the same form (118° to 120°); the two æthers are consequently isomorphous.—*Comptes Rendus*, Feb. 26, 1849.

On the Production of artificial Oil of Rue from Cod-Liver Oil. *By* Dr. Rudolph Wagner.

It is well known that cod-liver oil, when mixed with strong sulphuric acid, furnishes at first a purple-red tenacious mass, which colour almost immediately passes into a brownish-red, and then into a dark brown. If this mass is supersaturated with a caustic or carbonated alkali or an alkaline earth, and then heated, a penetrating odour of the essential oil of rue (*Ruta graveolens*) is disengaged. To procure the odoriferous substance in sufficient quantity for analysis, I mixed pretty considerable quantities of cod-liver oil and sulphuric acid, then saturated with potash or lime, and distilled with water. The water which passed over was turbid, and possessed an excessively strong odour of rue; but only in a few cases was I able to perceive any drops of oil upon its surface. Other experiments, in which I treated the fatty acids separated from the saponified cod-liver oil in a similar manner, furnished no better results. Fish oil and train oil from train-oil soap, submitted to a similar treatment, furnished the same result.

I am not able to state more of the oil obtained, than that it is of a light yellow colour, lighter than water, boils about 572°, and possesses the pure odour of the oil. With respect to the remarkable production of this oil from train oil by the action of sulphuric acid and subsequent saturation with a base, I may observe, that it certainly exists as such in the train oil, and cannot be considered as a product of decomposition by sulphuric acid. I found amongst the volatile fatty acids of cod-liver oil butyric and capric acids. Now if we bear in mind that Gerhardt has recently asserted that the oil of rue is the aldehyde of capric acid, $C^{20} H^{20} O^2$, which he rendered probable by converting it by treatment with nitric acid into a different acid of the formula $(C^2 H^2)^n + 4O$, pelargonic acid, we may be allowed to conclude that the sulphuric acid enters into a combination with the aldehyde of capric acid, or rather with the oxide of caprinyle, $C^{20} H^{19} O$, and that this compound is decomposed on the addition of a base, when aldehyde separates. This aldehyde, on becoming rancid, that is by the absorption of 2 equivs. oxygen,

forms capric acid, $C^{20} H^{19} O^3 + HO$. That the latter does not give rise to the production of the oil of rue is shown from the fact, that the capric acid is not at all altered by mixture with sulphuric acid.

The characteristic odour of the oil of rue or of the aldehyde of capric acid furnishes us with the means of detecting the presence of capric acid, or rather of the aldehyde, which always accompanies it. For instance, when fresh butter is heated with concentrated sulphuric acid, and potash is added in excess to the melted brown-red mass, the odour of the oil of rue is distinctly perceptible amidst the penetrating odours of the volatile fatty acids contained in the butter. I obtained the same odour by submitting to a similar treatment various sorts of fish oil, a piece of herring, several kinds of cheese, &c.

I will mention, in conclusion, that a mixture of train oil and sulphuric acid saturated with lime having been kept several days before distillation, the distillate consisted of a turbid water, which no longer possessed the odour of oil of rue, but very distinctly that of peppermint. This circumstance is interesting on account of the isomerism of the oil of rue with the camphor of the oil of peppermint.—*Journ. für Prakt. Chem.*, xlvi. p. 155.

On the Occurrence of Butyric Acid in the Fruit of the Soap-Tree (Sapindus saponaria), *with some Observations on the Volatile Acids of Tamarinds. By* Dr. Von Gorup-Besanez.

The *Sapindus saponaria* is a tree which attains the height of twenty to thirty feet in the West Indies and South America. The seeds of the fruit, pounded and softened in water, are used in India for washing linen. The peculiar odour led me to subject 2 lbs. of the fruit to distillation with water and sulphuric acid. I obtained a product, which, combined with soda and decomposed with sulphuric acid, furnished pure butyric acid. Two analyses of the silver salt gave 59·34 per cent. oxide of silver. Besides the butyric acid, there was some formic acid present.

Tamarind fruit, treated in a similar manner, furnished formic and acetic acids; but at the same time the distillate possessed an unmistakeable odour of butyric acid, without however my being able to detect the latter with certainty. As is well known, Nœllner obtained from crude tartar an acid which he called butyroacetic acid. Again, a solution of crystallized tartaric or citric acid contains after some time a considerable amount of acetic acid. Lastly, as experience has shown, both formic and butyric acids may be produced from tartaric acid under the influence of oxidizing agents. Now both the fruit of *Sapindus* as well as those of *Tamarindus Indica* contain tartaric acid; consequently there is nothing improbable in the assumption, that in the above cases it was the tartaric acid, which by absorption of oxygen was partially decomposed into formic, acetic and butyric acids—the different products predominating at different periods of the decomposition.—*Journ. für Prakt. Chem.*, xlvi. p. 151.

ANALYTICAL CHEMISTRY.

On the Estimation of Phosphoric Acid and on its Separation from Bases. *By* HENRY ROSE.

As is well known, the quantitative investigation of the compounds containing phosphoric acid is one of the most difficult problems of analytical chemistry. The difficulties increase with the number of bases with which the acid is combined; for the different phosphates, even when they all contain the same modification of the acid, the *c*-phosphoric acid, frequently behave very differently towards the same reagents, and are not all decomposed in the same manner when treated with one and the same decomposing agent.

The behaviour of the *a*- and *b*-phosphoric acids towards reagents differs in many cases so much from that of the ordinary phosphoric acid, that it is frequently necessary to employ other methods for their separation than for the estimation of the latter. It is however in most cases advantageous to convert those modifications into the ordinary phosphoric acid, which considerably facilitates the estimation of the acid.

It is especially in the investigation of the ashes of organic substances, which always contain phosphoric acid, often forming the most important constituent, that we meet difficulties in the estimation of this acid. Frequently the quantitative analyses of these ashes are so complicated, that their results, even though they have been obtained by chemists of high reputation, are not at all to be depended upon. The principal cause of these difficulties is undoubtedly owing to the circumstance, that we are acquainted with no method by which we are able to separate the phosphoric acid in a substance having a very complex composition, in such a manner that after its separation the other constituents may easily and accurately be estimated, as is the case for instance after separating sulphuric or hydrochloric acids, however large the number of bases or even of acids they may have been combined with. My principal object therefore in commencing this investigation was to discover some method by which the phosphoric acid might be so separated from mixtures of phosphates containing either modification of the acid, that not only its amount could be determined with the greatest accuracy, but that after its separation the bases might be readily examined and estimated without being contaminated by the reagent used to separate the phosphoric acid. I shall first briefly discuss the methods hitherto employed for the separation of phosphoric acid from bases, and comment upon their accuracy, and then proceed to describe the one I propose for this purpose.

Estimation of Phosphoric Acid.—When phosphoric acid is contained alone in solution, its amount may be best determined by evaporating the solution with a weighed quantity of recently-calcined oxide of lead, and igniting the dry mass. The solution must contain no bases, and only such acids besides phosphoric acid, as are completely expelled by heat from the oxide of lead, as nitric acid and others.

When phosphoric acid is contained in a liquid along with fixed or volatile bases and several other acids, it is usual to estimate it by precipitating it in the form of ammonio-phosphate of magnesia. In this operation far more precaution is requisite than when magnesia is separated by phosphate of soda and ammonia in the form of ammonio-phosphate of magnesia. It is above all things necessary that the acid is contained in the solution as *c*-phosphoric acid, for this only can be separated completely as ammonio-phosphate of magnesia. Moreover, when sulphate of magnesia, ammonia and a sufficient quantity of chloride of ammonium (to dissolve the hydrate of magnesia) have been added to the solution, it must not be heated strongly, much less boiled, otherwise a precipitate of hydrate of magnesia may result, but only warmed to 86°, and filtered after some hours. It is well known that the salt must not be washed with pure, but with water containing ammonia. The presence of a large amount of ammoniacal or other salts has no influence on the precipitation of the ammonio-phosphate of magnesia. M. Weber has shown how the *a*- and *b*-phosphoric acids may be converted into the *c* modification*.

When phosphoric acid is precipitated from a liquid as ammonio-phosphate of magnesia, it will not do to neutralize with carbonate of ammonia instead of with pure ammonia, for then ammonio-carbonate of magnesia is slowly deposited, frequently coating the sides of the glass in stellate groups of crystals. It may frequently contain no phosphoric acid, which only separates as ammonio-phosphate of magnesia on the addition of a certain amount of caustic ammonia†.

Separation of Bases from Phosphoric Acid by Sulphuret of Ammonium.

Those metallic oxides which are converted in their solutions or in the recently precipitated state by sulphuret of ammonium into sulphurets insoluble in an excess of the sulphuret of ammonium, are frequently separated by this reagent from phosphoric acid. When the mixture of the phosphates contains, besides such metallic oxides, magnesia or alkaline earths, these are precipitated as phosphates along with the sulphurets, on which account this method is only employed in the absence of these bases; but even in this case it is not frequently used, and mostly only in qualitative examinations, where it is often of advantage. Very frequently peroxide of iron is among the bases; and this, as is well known, is the most difficult of the sulphurets to separate.

To ascertain whether the peroxide of iron is wholly converted by sulphuret of ammonium into sulphuret of iron, and contains no residue of phosphoric acid, some basic phosphate of iron, Fe^2O^3,PO^5,

* Chem. Gaz., vol. v. p. 452.

† Different views prevail with regard to the composition of the salt which separates on adding a solution of carbonate of ammonia to a solution of sulphate of magnesia mixed with chloride of ammonium. M. Weber found it to consist in 100 parts—of magnesia, 21·35; ammonia, 7·07; carbonic acid, 30·15; and water, 41·43. This would agree best with the very complicated formula $5MgO\,CO^2+2NH^3\,CO^2+21HO$. The subject however deserves a more careful examination.

was dissolved in muriatic acid, the solution supersaturated with ammonia, and then mixed with sulphuret of ammonium; the precipitate was set aside for twenty-four hours, filtered, and then converted in the usual manner into peroxide of iron. The liquid filtered from the sulphuret of iron was precipitated as ammonio-phosphate of magnesia, without previously destroying the sulphuret of ammonium. M. Weber obtained in this way, in two analyses, the following results:—

	I.	II.	Calculated.
Peroxide of iron	49·31	51·47	52·31
Phosphoric acid	50·00	50·61	47·69
	99·31	102·08	100·00

It is evident from these experiments how difficult it is to separate the peroxide of iron from phosphoric acid by converting it into sulphuret. The sulphuret of iron proved on examination to be free from phosphoric acid, but the calcined phosphate of magnesia contained iron; on solution in muriatic acid, it gave out an odour of sulphuretted hydrogen; furnished with ammonia and sulphuret of ammonium, a gray precipitate; a blue colour with ferrocyanide of potassium; a red one with the sulphocyanide.

The result of this experiment will appear surprising, it being generally considered that metallic oxides are separated by no reagents so perfectly as by sulphuretted hydrogen or sulphuret of ammonium. It seemed probable that a better result might be obtained by converting the peroxide of iron in the phosphate into sulphuret in the dry way; such however is not the case, as shown by the following experiment made by M. Weber. Some phosphate of iron, Fe^2O^3, PO^5, was mixed with three times the amount of carbonate of soda and sulphur, and heated in a small porcelain crucible: it was not possible to fuse it with the strongest heat of an Argand lamp. On cooling, the mass, which had caked together, was treated with hot water, and the sulphuret of iron collected on a filter; the greater portion of it had a perfectly crystalline appearance, and pertinaciously resisted the action of muriatic acid; it must therefore have been a higher sulphuret, possessing probably the same composition as iron pyrites. Notwithstanding its crystalline structure, it could not be washed with pure water nor with dilute sulphuretted hydrogen, for the filtered water was of a greenish colour; it was requisite to employ water to which some sulphuret of ammonium had been added. On account of its insolubility in muriatic acid, it was calcined with access of air, then dissolved in muriatic acid and the peroxide of iron precipitated by ammonia; it proved to be perfectly free from phosphoric acid. The acid was precipitated in the usual way as ammonio-phosphate of magnesia; the following are the results:—

	I.	II.
Peroxide of iron.....	49·67	49·22
Phosphoric acid.....	48·85	46·83
	98·52	96·05

The sulphuret of iron is the most difficult of all to separate from a phosphatic liquid. With the other sulphurets this is far less the case.

Separation of Phosphoric Acid by Peroxide of Iron according to Berthier's Method.

This well-known method is frequently employed in quantitative investigations. It is founded on the circumstance that phosphoric acid in combination with peroxide of iron may be entirely precipitated by ammonia, but only when the oxide is present in a very large excess. Several experiments were made to ascertain what amount of peroxide of iron must be present in proportion to that of the phosphoric acid for the whole to be precipitated by ammonia. Berthier states that for 2 parts of phosphoric acid the peroxide of iron from 1 part of metallic iron is requisite. When too little of the solution of peroxide of iron is added to the liquid, so that no basic phosphate of iron can be formed, the perphosphate of iron is dissolved by the ammonia.

It is also of moment whether the acid is to be precipitated by the peroxide of iron as pyrophosphoric or as ordinary phosphoric acid. If, for instance, a solution of the pernitrate of iron is added to a solution of crystallized phosphate of soda, the weight of metallic iron being twice that of the phosphoric acid, and the mixture be then saturated with ammonia, the filtered liquid has a yellow colour. If as much peroxide of iron again be added, and the whole supersaturated with ammonia, the filtered liquid is, it is true, nearly colourless; but sulphuret of ammonium produces a green colour in the course of half an hour, if not immediately, and subsequently black flakes of sulphuret of iron are deposited. Moreover, when the precipitate is washed with cold water, it soon begins to pass yellow through the filter; and this occurs in a higher degree when ammoniacal water is employed; it then passes through with a perfectly dark red colour.

When the solution contains pyrophosphoric acid, a much larger amount of peroxide of iron is requisite to separate the acid—frequently eight to ten times the quantity prescribed by Berthier. We then finally obtain a liquid, which when filtered from the very bulky precipitate is clear and colourless, but on washing the precipitate the water passes through coloured frequently dark red. When boiling water is used, it passes through the filter perfectly clear at first; but as soon as it begins to cool upon the precipitate, it acquires a yellow, and finally a dark red colour.

When the solution of pernitrate of iron is added to a solution of the pyrophosphate of soda, a white precipitate is produced (even when the solution of iron contains much free nitric acid), which does not readily dissolve on the addition of a larger quantity of nitric acid; but it is soluble in hydrochloric acid. On supersaturating with ammonia, a perfectly transparent red solution is formed when no more peroxide of iron has been employed than directed by Berthier. It is only on the addition of a much larger amount of

peroxide of iron that a brownish-red precipitate is produced by ammonia. On the addition of a solution of nitrate of iron containing free nitric acid to a solution of a *c*-phosphate, no precipitate is produced until after supersaturation with ammonia.

It is evident from these experiments that Berthier's method cannot be employed in accurate investigations; it may however sometimes be of use in qualitative experiments.

Von Kobell has ingeniously modified Berthier's method. Whilst according to the method of Berthier (even were it capable of affording a correct result) the phosphoric acid can only be separated from a liquid containing sulphuric, nitric or hydrochloric acid and alkalies, but no other bases, it can be separated by Kobell's plan from magnesia and from all those metallic oxides which belong to the strong bases and are not precipitated in the cold by carbonate of baryta. This method consists in dissolving the phosphatic compound in hydrochloric acid, adding to it a solution of the peroxide of iron, and mixing the whole in the cold with an excess of carbonate of baryta instead of with ammonia; the whole of the phosphoric acid combined with peroxide of iron is precipitated by the carbonated earth, whilst the metallic oxide is held in solution combined with hydrochloric acid. Von Kobell recommends carbonate of lime; carbonate of baryta however is preferable.

When the amount of peroxide of iron added is known, it is merely requisite to dissolve the washed and gently-calcined precipitate, and to precipitate the baryta from the solution by sulphuric acid, in order to calculate from the weight of the sulphate of baryta the amount of carbonate of baryta, which will then furnish the amount of phosphoric acid. The baryta dissolved in the liquid separated from the precipitate is removed by sulphuric acid, and the amount of base which had been combined with the phosphoric acid determined.

This method furnishes satisfactory results. 1·965 grm. calcined phosphate of magnesia was dissolved in hydrochloric acid, and to it was added a solution of 1·284 grm. metallic iron in nitromuriatic acid, and then an excess of carbonate of baryta. A very slight precipitate is produced with concentrated solutions, but on dilution with water a bulky light brown precipitate is deposited. The filtered liquid, freed from baryta by sulphuric acid, furnished with phosphate of soda and ammonia 2·005 grms. calcined phosphate of magnesia. A small excess therefore was obtained; it consisted of peroxide of iron, which had not been entirely removed by the carbonate of baryta. The solution of the calcined precipitate gave a gray precipitate with ammonia and sulphuret of ammonium; but the presence of iron was still more distinctly indicated by sulphocyanide of potassium.

As the precipitate produced by carbonate of baryta is very bulky, Von Kobell proposes, when the object is a mere separation, to treat the phosphate, if the base is insoluble in a solution of hydrate of potash, previously with this reagent in order to remove the greater portion of the phosphoric acid. Only a very small quantity of solution of iron need then be added to the compound treated with potash, and the precipitate is less bulky.

Separation of Phosphoric Acid by Carbonate of Baryta.

As the separation of phosphoric acid according to Kobell's method succeeded tolerably well, I attempted to separate the strong bases from phosphoric acid by carbonate of baryta without any addition of solution of iron: I did not expect to succeed, as phosphoric acid is not perfectly precipitated from its aqueous solution by carbonate of baryta; the result however was favourable beyond all expectation. 1·229 grm. calcined phosphate of magnesia was dissolved in muriatic acid, the solution left in contact with carbonate of baryta for a long time at the ordinary temperature, filtered and washed with cold water. The precipitate dissolved in muriatic acid gave, after removing the baryta with sulphuric acid, on the addition of sulphate of magnesia, chloride of ammonium and ammonia, 1·216 grm. calcined phosphate of magnesia. The liquid separated from the precipitate, after removing the baryta by sulphuric acid, furnished, on precipitation with phosphate of soda and ammonia, 1·290 grm. calcined phosphate of magnesia.

Both the quantities of the calcined phosphate of magnesia obtained in the analysis should be equal, and likewise agree with the quantity taken for analysis. They do not however differ very considerably. The loss in phosphoric acid was owing to the acid of the pyrophosphate of magnesia employed not being entirely converted into *c*-phosphoric acid by solution in muriatic acid. The results were—

	Found.	Calculated.
Magnesia	36·95	36·61
Phosphoric acid	62·49	63·39

Separation of Phosphoric Acid by fusing Phosphatic Compounds with Carbonated Alkali.

A large number of phosphates are completely decomposed by fusion with carbonated alkali. On treating the fused mass with water, only the excess of carbonate and the phosphated alkali are dissolved, when the bases combined with the phosphoric acid are insoluble in the solution of the carbonated alkali. Precisely those phosphates which most frequently occur in investigations, especially in the examination of the ashes of organic substances, are not completely decomposed by fusion with carbonated alkali; these are the combinations of phosphoric acid with the alkaline earths, and especially the *phosphate of lime*. I have frequently fused this salt with carbonate of potash as well as with carbonate of soda, and with a mixture of the two, but have never effected a complete decomposition, however varied the proportions and the degree of heat. The amount of decomposed phosphate of lime differed considerably in the several experiments; sometimes the residue of the fused mass, insoluble water, only contained a very little carbonate of lime.

Nor can the phosphate of lime be perfectly decomposed by treatment with a solution of carbonate of soda. When it is treated with a concentrated solution of a carbonated alkali in the cold in the non-calcined state, the decomposition is nearly perfect. When the insoluble portion is well washed, but a slight precipitate of phosphate

of lime is produced in the muriatic solution by ammonia. A solution of phosphate of soda consequently exerts no action in the cold upon carbonate of lime. When, on the other hand, calcined phosphate of lime is treated with a solution of carbonate of soda, the decomposition is imperfect; 1·455 grm. ignited phosphate of lime, $2CaO, PO^5$, boiled several hours with a solution of carbonate of soda, was dissolved after perfect washing in dilute muriatic acid. The solution furnished, on saturation with ammonia, 0·620 grm. phosphate of lime; consequently 42·61 per cent. of the phosphate of lime had not been decomposed by boiling with carbonate of soda. When however calcined phosphate of lime is treated in the cold with a solution of carbonate of soda, scarcely any decomposition occurs. When filtered after seven days, the liquid, supersaturated with muriatic acid and mixed with sulphate of magnesia, chloride of ammonium and ammonia, exhibited scarcely any perceptible turbidness.

When phosphate of lime is fused in a silver crucible with hydrate of potash, it dissolves entirely on ignition to a clear liquid; but on treating the fused mass with water, nearly the whole of the phosphate of lime is left undissolved; and on supersaturating the filtered liquid with an acid, then mixing it with sulphate of magnesia, chloride of ammonium and ammonia, a very slight precipitate of ammonio-phosphate of magnesia is obtained.

Phosphate of Strontia, when fused with carbonate of soda, is partially but not entirely decomposed. When the fused mass is treated with water, the liquid gives but a slight precipitate on supersaturation with muriatic acid, and the addition of sulphate of magnesia, chloride of ammonium and ammonia.

Phosphate of Baryta, on the contrary, is decomposed to a far greater extent, although not completely. It fuses with six times its weight of carbonate of soda. When treated with water, the insoluble and washed residue dissolves with great effervescence in muriatic acid; the solution gives with ammonia only a slight precipitate of phosphate of baryta.

Phosphate of Magnesia requires six times its weight of carbonate of soda to fuse the mass. In this case the decomposition is nearly complete; and according to several experiments, not more than from 2 to 3 per cent. of phosphate of magnesia remain undecomposed; according to Heintz, perfect decomposition obtains when the fusion is effected in a blast-furnace.

When a mixture of carbonate of potash and soda in equivalent proportions is used for the decomposition of the phosphate of magnesia, the mixture fuses with the greatest ease, and the decomposition is, according to M. Weber, complete. It is however impossible to effect by means of this mixture, a perfect decomposition of the phosphates of baryta, strontia and lime; in this, as in the previous instance, the phosphate of lime least of all.

Phosphate of Zinc is completely decomposed with carbonate of soda; the mass, treated with water and filtered, furnishes a liquid in which no oxide of zinc can be detected by sulphuret of ammo-

nium. The insoluble oxide of zinc was also free from phosphoric acid.

Phosphate of the Protoxide of Manganese is likewise completely decomposed by fusion with carbonate of soda. A brown residue is obtained on treating the fused mass with water which contains much sesquioxide of manganese; and after being well washed, furnishes a very dark brown solution with muriatic acid, which is rendered colourless by boiling. Ammonia produces a white precipitate, which is soluble in a large amount of chloride of ammonium, in which solution sulphate of magnesia produces no precipitate. Sulphuret of ammonium produces no precipitate of sulphuret of manganese in the liquid filtered from the insoluble residue.

Phosphate of Copper is partially reduced on fusion with carbonate of soda to protoxide of copper; the insoluble residue left on treatment with water disengages deutoxide of nitrogen on solution in nitric acid. The acid solution, supersaturated with ammonia, is not rendered turbid by sulphate of magnesia and chloride of ammonium; the liquid filtered from the insoluble residue, after being rendered acid with nitric acid, furnished on supersaturation with ammonia a slight turbidness, and exhibited a faint bluish tint. We know that oxide of copper cannot be entirely precipitated by carbonated alkali even in the moist way.

Phosphate of the Peroxide of Iron is completely decomposed by fusion with carbonate of soda. When the fused mass is treated with water, the washed peroxide of iron contains not a trace of phosphoric acid; for on solution in muriatic acid, not the slightest precipitate is produced on the addition of tartaric acid, chloride of ammonium, sulphate of magnesia and ammonia.

1·764 grm. perphosphate of iron, Fe^2O^3, PO^5, fused with four times its weight of carbonate of soda, gave, on treating the fused mass with water, 0·938 grm. peroxide of iron, which, dissolved in muriatic acid and precipitated from the solution with ammonia, weighed only 0·923. The liquid separated from the peroxide of iron, rendered acid, then saturated with ammonia and mixed with sulphate of magnesia and chloride of ammonium, gave 1·320 grm. calcined phosphate of magnesia. There was obtained therefore in 100 parts—

	Found.	Calculated according to Fe^2O^3, PO^5.
Peroxide of iron.....	52·32	52·31
Phosphoric acid.....	47·78	47·69

The result is very accurate, and the method of decomposing the phosphate of iron by fusion with carbonate of soda far preferable to treating the solution in acids with sulphuret of ammonium.

Although it is evident from the above experiments that several phosphates, especially those of the true metallic oxides, may be entirely decomposed by fusion with carbonated alkali, others, on the contrary, are only partially decomposed. When consequently we have a mixture of phosphates to examine, and wish to separate the phosphoric acid from the bases, in order to examine the latter with-

out the fear of their retaining more or less phosphoric acid, the fusion with carbonated alkali is not adapted. If alkalies were contained among the bases, they could not be determined.

But since phosphoric acid can be easily and perfectly separated by fusion with carbonate of soda from those metallic oxides which are insoluble in alkaline carbonates, this method was also tried in the separation of phosphoric acid from those metallic oxides and acids which dissolve in alkaline carbonates, but are converted by reduction into oxides which are insoluble in it. The most favourable results were obtained.

Separation of Phosphoric Acid from Oxide of Uranium.

When phosphate of the oxide of uranium is fused with carbonated alkali, the result is not trustworthy, especially when a considerable excess of the carbonate has been used, as on treating the fused mass with water some oxide of uranium is always dissolved with the phosphate and carbonated alkali. Perfect decomposition is not effected by boiling with concentrated solution of potash.

In the methods recently described by M. Werther* there is always the danger of destroying the platinum crucible. The following plan of separating phosphoric acid from oxide of uranium is far more simple:—The compound is mixed with three times its weight of carbonate of soda and as much cyanide of potassium, and the whole fused in a platinum crucible. At first a very moderate heat must be applied, as the mass froths considerably and shows an inclination to overflow. However, this ceases after a little time, when a stronger heat is applied until the whole is fused to a clear liquid mass. Whilst the whole is liquid a small piece of cyanide of potassium is placed upon it, the lamp immediately removed, and the crucible covered. On adding the cyanide of potassium, the lid should be held close over the crucible, to prevent any loss from ejection. On cooling, the crucible is placed in a beaker, digested with hot water until the mass is softened, and the insoluble portion allowed to subside. It is advisable to add some chloride of ammonium to the liquid, as this causes the suspended protoxide of uranium to subside, and prevents the liquid from passing turbid through the filter. The protoxide of uranium is washed with water containing a little chloride of ammonium.

The dried protoxide of uranium easily becomes yellow on ignition, even in a covered crucible, which is owing to its containing some alkali; but when it is calcined in an atmosphere of hydrogen, it is obtained of constant weight. However, since it contains alkali, it must be dissolved in nitric acid; the oxide of uranium precipitated with ammonia, and washed with water to which a few drops of chloride of ammonium have been added. When calcined after drying in an atmosphere of hydrogen, less protoxide of uranium is obtained than previously; and in the liquid filtered from the precipitate minute quantities of the alkali can be detected.

The liquid filtered from the protoxide of uranium, which contains

* Chem. Gaz., vol. vi. p. 329.

besides the whole amount of phosphate, carbonate of soda and cyanide of potassium, is supersaturated with hydrochloric acid, and the phosphoric acid precipitated as ammonio-phosphate of magnesia.

This method furnishes very accurate results, as will be seen by the following experiment:—1·085 grm. protoperoxide of uranium ($UO+U^2O^3$), corresponding to 1·042 UO, was mixed with 0·714 calcined phosphate of soda, which contains 0·381 phosphoric acid; the mixture contained therefore 57·90 per cent. UO and 21·19 PO^5. There was obtained 1·071 grm. or 59·56 per cent. UO, which however, by solution in nitric acid and precipitating the oxide of uranium as above described, was diminished to 1·039 grm. (=57·78 per cent.); the amount of calcined phosphate of magnesia obtained was 0·608 grm., corresponding to 0·359 grm. phosphoric acid, or 20·00 per cent.

Separation of Phosphoric Acid from Chromic Acid.

Earlier experiments on the separation of these two acids, in which the chromic acid was reduced to oxide of chromium, which can then be separated by fusion with carbonate of soda from the phosphoric acid, did not furnish perfectly accurate results, because it is difficult to reduce the last traces of chromic acid to the state of oxide. The method employed for separating the oxide of uranium from phosphoric acid by means of cyanide of potassium, was employed with advantage.

0·957 chromate of potash and 0·451 phosphate of soda, mixed with three times the quantity of carbonate of soda and cyanide of potassium, was fused; the fused mass, treated with water, furnished a green insoluble oxide of chromium. For the better separation of the oxide of chromium, the perfectly colourless liquid was mixed with chloride of ammonium, with a weak solution of which the oxide was washed. The filtered liquid, carefully supersaturated with muriatic acid, then mixed with ammonia, sulphate of magnesia and chloride of ammonium, furnished ammonio-phosphate of magnesia, which weighed on ignition 0·375 grm., corresponding to 16·90 phosphoric acid in the mixture, which contained according to theory 17·47. The calcined oxide of chromium weighed 0·401 grm., which corresponds to 37·85 per cent. chromic acid, whilst the calculated quantity is only 35·01 per cent. It evidently contained alkali.

To ascertain this, the calcined oxide of chromium was digested and heated with concentrated sulphuric acid, in which, as is well known, it does not dissolve, at all events not to any extent, whilst on dilution with water the insoluble oxide assumes a very flocculent and bulky consistence, so that it appeared probable it might be separated in a pure state by treatment with ammonia and a gentle heat; but the oxide weighed after ignition and after treatment with carbonate of ammonia 0·401 grm., or just as much as before treatment with sulphuric acid. It was therefore fused with a mixture of carbonate and nitrate of alkali, the fused mass dissolved in water, the solution neutralized with nitric acid, and the chromic acid precipitated as chromate of the protoxide of mercury, which left on cal-

cination only 0·375 oxide of chromium, corresponding to 34·51 per cent. chromic acid. This is half a per cent. less than theory requires; and it will not appear remarkable, considering how many operations the oxide of chromium had to be submitted to, to convert it into pure oxide. The presence of the alkali could be detected in the liquid separated from the protochromate of mercury.

The separation of phosphoric acid from chromic acid might certainly be most easily effected by precipitating the phosphoric acid from the solution as ammonio-phosphate of magnesia; but then it is difficult to separate the chromic acid from the magnesia; it is best accomplished by the protonitrate of mercury, on which account the method of fusion with carbonate of soda and cyanide of potassium is preferable.

[To be continued.]

PROCEEDINGS OF SOCIETIES.

Institution of Civil Engineers.

April 17th, 1849.

(Mr. R. Stephenson, V.P., in the Chair.)

"On an Application of certain Liquid Hydrocarbons to Artificial Illumination," by Mr. C. B. Mansfield.

The system proposed by the author (which was illustrated in the room by a working apparatus) consisted in conducting a stream of almost any gas, or even of atmospheric air, through a reservoir charged with benzole (a liquid hydrocarbon procured from coal tar) or some other equally volatile hydrocarbon; the gas or air so naphthalized being then conducted, like common coal gas, through pipes to the burners. It was stated that the system was applicable on any scale, from the dimensions of town gas works to the compass of a table-lamp. In the apparatus exhibited, a small gas-holder, filled by a pair of bellows, supplied common air through pipes. The gases formed by passing steam over red-hot coke would answer well for this purpose; and it would depend on local circumstances whether this mode of generating the current would be preferable to the expenditure of the mechanical force necessary for driving atmospheric air through the pipes. Pure oxygen charged with the vapour would explode on ignition; it was therefore suggested that this might prove a useful source of motive force. It was however stated to be difficult to form an explosive mixture of the vapour with common air. By decomposing water with the voltaic battery, naphthalizing the hydrogen with benzole, and burning it with the aid of the equivalently-liberated oxygen, a simple light of intense power might be obtained. The system was shown to be a great simplification of the ordinary system of gas-lighting, as no retorts, refrigerators, purifiers or meters were required, and the products of combustion were as pure as those from the finest wax. It was expected that the elegance of the material and the simplicity of the apparatus

would induce its introduction into buildings and apartments where coal gas was not now considered admissible. The apparatus and conditions necessary for the success of the method were, a flow of cheap gas, or of air, driven through pipes by any known motive power, and a reservoir of the volatile spirit through which the main pipe must pass in some convenient part of its course, these pipes and reservoirs being protected from the cold. It was stated, that though the liquid did not require to be heated above the average temperature of the air, it was liable to become cooled by its own evaporation, so as to require an artificial supply of warmth. This was readily effected by causing a small jet of flame of the gas itself to play upon the reservoir, and by a simple contrivance, called a "thermostat," by which the flame was shut off when necessary, the temperature could be made self-regulating, so as never to rise above or fall below a proper degree. The cooling due to the evaporation would of course be inversely proportionate to the quantity of liquid in the reservoir. If atmospheric air was used as the vehicle for the vapour, the jet-holes in the burner, from which it escaped for combustion, must be slightly larger than those for coal gas. Some burners, contrived for the purpose of accurately adjusting the size of the orifice to the quantity of luminiferous matter escaping, were exhibited and described; they were made so, that by moving a part of the burner, any required quality of flame, from lightless blue to smoky, could be obtained, there being a medium point at which the most perfect brilliancy was arrived at. The burners would answer equally well for coal gas, though that material could not, even by them, be made to evolve so white and pure a light as that from benzole vapour.

In conclusion, some data were given on which a calculation of price was founded. It was stated, that a gallon of benzole, of the degree of purity requisite for the purpose, would cost about two shillings and sixpence; to this the expense of the air-current and the interest of the original outlay on apparatus were to be added. This, the author presumed, would not raise the cost to more than four shillings for the consumption of a gallon of benzole. It was stated that one ounce of that liquid would give a light equal to four wax candles, of four to the pound, for one hour; or one gallon for about one hundred and twenty hours. It was inferred, that a gallon of this material was equivalent to about one thousand cubic feet of coal gas.

Finally, for comparison with coal gas at a distance from the mines, it was stated, that while to produce one thousand cubic feet of gas at least two hundred pounds of coal must be transported, one gallon of benzole did not weigh more than seven pounds; this, in carriage, would give benzole an advantage of twenty-eight to one over coal as a source of light.

In the discussion which ensued, high encomiums were passed upon the talent and patient labour exhibited by Mr. Mansfield in the investigation of this important subject, which promised to lead to most remarkable results, as an extension of gas-lighting to positions where it had not before been considered applicable.

THE CHEMICAL GAZETTE.

No. CLVIII.—May 15, 1849.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Further Observations on the Spontaneous Decomposition of Ox-Bile. By Prof. BUCHNER, Jun.

THE following preliminary notices will appear highly interesting in connexion with the results of Strecker's investigation on the bile* and Redtenbacher's on taurine†. According to the results of those investigations, we were led to view,—1st, the pure bile to be simply a choleate and cholate of soda (Strecker); and 2nd, taurine to be isomeric with bisulphate of aldehyde-ammonia. M. Buchner observes, with regard to the first, that in whatever way we view the constitution of the bile, so much is certain, that the products of its spontaneous decomposition (caused by the putrefying mucus of the bile, according to former researches of the author and Gorup-Besanez) are at the commencement not very numerous. This decomposition consists simply in a separation of the principal constituent of the bile into

I.

Taurine ..... } substances containing sulphur and nitrogen,
Ammonia..... }

and

II.

Choloidic acid.. } substances free from sulphur and nitrogen,
Cholalic acid .. }

of which the last acids, according to the duration of the putrefaction, are formed in different proportions, and are combined with the soda of the bile and the generated ammonia.

With respect to the second point, the author states that the taurine disappears by further putrefaction; and after the formation of an intermediate product, a lower oxide of sulphur, sulphate of soda, may be detected among the products of decomposition of the bile. Whilst taurine is found in the bile after it has been allowed to putrefy from one to two months only, sulphate of soda is found after the lapse of six months. The brown mother-liquor from which the sulphate of soda has crystallized disengages, when saturated with muriatic acid, sulphurous acid, and deposits some free sulphur, arising from the decomposition of a hyposulphite, or perhaps at the

* Chem. Gaz., p. 49 of the present volume. † *Ibid.*, vol. vi. p. 69.

same time of a sulphite. The hyposulphite may have been formed by the oxidation of the hydrosulphate of ammonia, which is found in putrescent bile; and both may be secondary products, and the sulphurous acid be an immediate product of decomposition, which is still undetermined. It must also be remembered, with respect to the constitution of the bile according to Redtenbacher, that Gorup-Besanez detected acetic acid among the products of putrefaction of purified bile which had been exposed for several months to the air. The author has moreover found some other allied acids, especially valerianic acid.

The sulphate of soda which is found after the putrefaction is not present in the fresh bile. Since, according to the observations of Dr. Schmidt and Buchner, the portal blood contains more sulphates than that drawn from the jugular vein, it appears to result from these two facts that the sulphates are used for the production of a very essential constituent of the bile.—*Gel. Anz. d. k. Bair. Acad.*, No. 232.

On Carbanilic Acid and the Carbanilates. *By* G. Chancel.

In a former notice*, I showed that under the influence of the hydrosulphate of ammonia nitrobenzamide is converted into a new substance, *anilamic urea*, to which I assigned the name of *carbanilamide*. I showed that when carbanilamide is heated, there is disengaged at first ammonia, and subsequently at a higher temperature pure aniline. As I suspected, the two following phases must be distinguished in this metamorphosis by potash:—

First phase.... $C^7 H^8 N^2 O + O(KH) = H^3 N + C^7 H^6 KNO^2$.
Carbanilamide. Carbanilate of potash.

Second phase.. $C^7 H^6 KNO^2 + O(KH) = C^6 H^7 N + CO^3 K^2$.

The carbanilamide is, in fact, converted with the greatest ease into carbanilate of potash. It is merely requisite to boil this substance with a concentrated solution of caustic potash until no more ammonia is evolved, and then to add an excess of acetic acid. If the liquid is not very concentrated, no precipitate results; and the carbanilic acid is deposited on cooling in orange-coloured crystals, which are purified by recrystallization.

This acid exhibits some very characteristic reactions, and furnishes crystalline salts. Its composition and its metamorphoses prove clearly that it must be viewed as the bicarbonate of aniline minus the elements of 1 equiv. water,—

$$(CH^3 O^3, C^6 H^7 N) - H^2 O = C^7 H^7 NO^2;$$

for the alkaline and earthy carbanilates, when heated with potash or caustic baryta, are converted into carbonates and aniline. When carbanilic acid is heated suddenly with spongy platinum, it is resolved into carbonic acid gas and aniline; sulphuric acid converts it into sulphanilic acid.

* Page 173 of the present volume.

The composition of carbanilic acid has been determined by the analysis of the acid and of the salt of silver; it is expressed by the formula $C^7 H^7 NO^2$. The carbanilate of silver is nearly insoluble in cold water, tolerably soluble in hot, from which it is obtained in beautiful crystals by cooling. It is not altered at 212°, and may be perfectly dried; but at a higher temperature it is decomposed. Its composition accurately corresponds with the formula $C^7 H^6 AgNO^2$.

It is seen therefore that carbanilic acid is a monobasic acid, that is to say, capable of exchanging 1 equiv. of hydrogen for 1 equiv. of metal. Its metamorphoses moreover prove that it is a conjugate acid, formed by the union of 1 equiv. aniline and 1 equiv. carbonic acid, with the elimination of 1 equiv. water.

I should observe, in concluding, that carbanilic acid obtained by the action of potash upon carbanilamide appears to be identical with the benzamic acid of M. Zinin, and even with the anthranilic acid of M. Fritzsche; however, I merely mention this opinion with a certain reserve, comparative experiments being still wanting; but, at all events, if these acids are not absolutely identical, they are very nearly allied. It is evident that they are more than isomerous, for they all possess the same fundamental properties, and are metamorphosed in the same manner under the influence of reagents. It will therefore be necessary to regard them as varieties of one and the same chemical species, of which we have more than one example in chemistry. I need merely mention tartaric, metatartaric and paratartaric acids, which are isomerous, have the same capacity of saturation, and are decomposed in the same manner under the influence of powerful reagents. I intend shortly to publish some comparative observations on anthranilic, benzamic and carbanilic acids.—*Comptes Rendus*, March 26, 1849.

On the Change which a Solution of the Protosulphate of Iron experiences by exposure to the Air. *By* G. C. Wittstein.

It is generally admitted that a solution of the protosulphate of iron deposits on exposure to the air $2Fe^2O^3 + SO^3$; which however is not the case according to the author's experiments. A solution of 1 part protosulphate of iron in 4 parts water, exposed for eleven months in a loosely covered vessel, deposited a precipitate, which gave on analysis—

Peroxide of iron	46·50	46·30	2 =	45·45
Sulphuric acid	33·19	33·43	3	34·10
Water	20·31	20·27	8	20·45

According to this the precipitate is $2Fe^2O^3 + 3SO^3 + 8HO$. The liquid filtered from this precipitate deposited a further precipitate in the course of four weeks, which had exactly the same composition. The liquid filtered from this second precipitate still contained a large amount of protosalt, although not more than half an ounce had been taken for the experiment. After fifteen months scarcely a third part had become converted into a persalt.—Buchner's *Repert.*, i. p. 182.

On the supposed Hydrurets of Silver and some other Metals. *By* M. Poggendorff.

It has long been observed, that when a weak solution of nitrate of silver is decomposed by the battery, a black powder is deposited at the negative pole. This powder had been considered to be a combination of silver with hydrogen, a true hydruret of silver, by Priestley, Ritter, Brugnatelli and Ruhland. The author has repeated the experiments of these observers, and has not arrived at the same results. Having placed two slips of platina in a solution of nitrate or of sulphate of silver, he connected them with the two poles of a small battery consisting of two of Grove's cells; and he observed that the negative plate became coated with a black precipitate, which was nothing but metallic silver. This fact is placed beyond all doubt by M. Poggendorff. We will only enumerate the two following experiments.

When the negative plate has become coated with the black precipitate in question, and the current is discontinued without touching the plate, the black colour of the precipitate suddenly changes to a grayish-white, the ordinary colour of finely divided silver, without the least disengagement of gas being perceptible.

When a stratum of mercury is used as the negative pole in the decomposition of the nitrate of silver, in proportion as the black powder is deposited on the surface of the mercury, it is absorbed by it, forming an amalgam, without any disengagement of gas. It is well proved therefore that this black powder is metallic silver, and that the hydruret of silver does not exist, or at least is not formed under these circumstances. The same must be said with regard to the hydrurets of bismuth, antimony and tellurium. M. Poggendorff succeeded only in forming a single hydruret by electrical decomposition, the hydruret of copper which M. Wurtz had previously obtained by decomposing a solution of sulphate of copper with an excess of hypophosphorous acid.—Poggendorff's *Annalen*, lxxv. p. 337.

On the Amount of Water contained in Phosphate of Soda. *By* Prof. R. F. Marchand.

Twenty-one years ago Clark described this salt as containing 25 equivs. of water, 24 of which were expelled at a gentle heat; the last however only on calcination. Recently Malaguti has asserted that this salt contains 27 equivs. of water. Berzelius considered it possible that the latter amount might be peculiar to a salt which had crystallized from a cold solution, as Setterberger had found that the arseniate crystallized at 32° contains 27 equivs. water. Marchand's experiments show that this salt contains, as stated by Clark, Graham and Fresenius, only 25 equivs., and that the existence of a salt with 27 atoms of water, corresponding to Setterberger's arseniate, is extremely doubtful.—*Journ. für Prakt. Chem.*, xliv. p. 172.

On the Essential Oil of Turpentine and Isomeric Compounds. *By* H. Deville.

The principal object of this investigation is the study of the curious properties which distinguish that class of hydrocarbonaceous compounds to which the name of hydrates of essential oils has been given. My first object was to examine as completely as possible the hydrate of the essential oil of turpentine, which is the most easily obtained of these bodies. I have found that this substance, the composition of which is represented by the formula $C^{20}H^{16}$, H^6O^6, loses 2 equivs. of water at a temperature scarcely higher than 212°, or by exposure *in vacuo*, and is converted into a hydrate with 4 equivs. of water, $C^{20}H^{16}$, H^4O^4. But this, in whatever manner prepared, very rapidly absorbs from the moist atmosphere the amount of water requisite to pass into its primitive state. This fact will appear rather difficult to explain, when it is known that both these hydrates are nearly insoluble in water.

With hydrochloric acid these hydrates furnish water, and an artificial camphor, possessing all the properties of the camphor from the essential oil of lemon, with the same melting-point and the same composition. Moreover, this hydrochlorate furnishes, when treated with potassium, an essential oil, which it is impossible to distinguish from the essential oil of lemon by its odour, its boiling-point, density and composition. I believe therefore that the problem of the conversion of the essential oil of turpentine into the essential oil of lemon is solved by this experiment.—*Comptes Rendus*, March 26, 1849.

On the Precipitation of Phosphoric Acid by Baryta. *By* Prof. Wackenroder.

The author communicates a series of experiments upon the solubility and nature of the phosphate of baryta, which were made with a view to ascertain the accuracy, and indeed the applicability, of baryta for precipitating phosphoric acid. According to the author, phosphoric acid can be entirely precipitated by chloride of barium from an aqueous solution of the alkaline *c*-phosphates, in which carbonate and sulphate of potash, chloride of sodium or potassium may be contained. On dissolving the mixed precipitate of carbonate, sulphate and phosphate of baryta in very dilute nitric acid, sulphate of baryta remains, which must be purified with muriatic acid to obtain the correct amount of sulphuric acid. The phosphate of baryta is precipitated from the nitric solution by ammonia, except a mere trace. This phosphate of baryta, when not washed too long with water, and calculated after calcination as $5BaO+2PO^5$, gives very accurately the amount of phosphoric acid which was contained in the solution. The dry precipitate appears to consist of 2 atoms of bibasic *c*-phosphate of baryta and 1 atom of nitrate of baryta $=2(2BaO, HO+PO^5)+(BaO+N^2O^5)$, from which is formed by

calcination $5BaO+2PO^5$. The analysis of this precipitate furnished—

Baryta.....	72·337	5 =	479·017	72·835
Phosphoric acid ..	27·663	2	178·662	27·165

Archiv der Pharm., lvii. p. 17.

On the Neutral Sulphate of the Oxide of Ethyle and the Products of its Decomposition. By Dr. Charles M. Wetherill.

Although the neutral sulphate of the oxide of ethyle, the true sulphuric æther, has been sought for in vain, and doubtless often formed, Dr. Wetherill has first succeeded in isolating it and studying its properties. It is prepared by slowly passing the vapours of anhydrous sulphuric acid into pure æther surrounded by ice and salt; agitating the mixture with 1 vol. æther and 4 vols. water, separating the two strata of liquids, agitating the ætherial solution with milk of lime, washing with water and distilling off the æther. The oily liquid in the retort is transferred to a capsule, washed with a little water, and dried *in vacuo* over oil of vitriol. The aqueous solution contains sulphurous, ethionic and sulphovinic acids; and if the temperature were not kept low, it contains in addition isethionic and methionic acids.

When pure, the neutral sulphate is a colourless oily liquid, of a pungent taste and peppermint odour; spec. grav. 1·12; distils with great difficulty, even in an atmosphere of carbonic acid; the distillate is colourless, neutral and heavier than water. Chlorine is dissolved by it in the cold without decomposition, giving a green colour, and the oil is again precipitated by water. A solution of potash, saturated with sulphuretted hydrogen, changes it into mercaptan and sulphate of potash—

$$C^4 H^5 O, SO^3 + KS, HS = C^4 H^5 S, HS + KO, SO^3.$$

It dissolves without alteration in fuming nitric acid; but by adding potash and heating, nitrous æther is formed ($C^4 H^5 O, NO^3$). Treated with muriatic acid and potash, a heavy oil distils over with an odour of apples. With water the oil disappears entirely, leaving an acid solution. The carbon and hydrogen were determined by combustion with oxide of copper, with chromate of lead and with a mixture of oxide of copper and chlorate of potash; the sulphuric acid by chloride of barium. The result was $C^4 H^5 O, SO^3$.

By the action of water aided by heat the oil entirely disappears; and if carbonate of baryta be added and the filtered solution be evaporated, crystals of methionate of baryta separate, and the remainder of this salt is thrown down by alcohol. The methionate is proved by its properties and analysis. The mother-liquor yields a salt soluble in alcohol, which is shown to be an equal mixture of sulphovinate and isethionate of baryta by analysis and behaviour; for sulphovinic acid is resolved by boiling into sulphuric acid and alcohol, while the latter is not. By determining the baryta in the

mixture, boiling the acids, removing the free acid by carbonate of baryta, and determining the baryta in the last solution of isethionate, the weight of the former is found to be about double that of the latter.

It follows from these experiments, that the usual explanation of the formation of heavy oil of wine, previous to that of ethionic acid, is erroneous; for not the slightest trace of the heavy oil of wine is found in the substance resulting from the action of anhydrous sulphuric acid on æther or alcohol. The probable rationale is, that the anhydrous sulphuric acid partly forms directly the neutral sulphate of æther ($C^4 H^5 O, SO^3$), and partly decomposes the æther, forming Regnault's sulphate of olefiant gas ($4SO^3, C^4 H^4$), which takes up 1 equiv. water to form ethionic acid ($4SO^3, C^4 H^5 O$). Another portion of the acid takes up water and unites with æther, producing sulphovinic acid ($C^4 H^5 O, 2SO^3, HO$). In the case of alcohol, part of the sulphuric acid takes up water and unites with a portion of alcohol, forming hydrated sulphovinic acid, while the liberated æther partly forms the neutral sulphate and partly ethionic acid. The products of decomposition sufficiently distinguish the neutral sulphate from the heavy oil of wine. 4 equivs. of the neutral sulphate with 3 equivs. water are first resolved into ethionic acid and 3 equivs. alcohol, and by the action of heat into isethionic and sulphovinic acids and alcohol, as shown in the following equation:—

$$4(C^4 HO, SO^3) + 3HO = C^4 H^5 O, 4SO^3 + 3(C^4 H^5 O, HO)$$
$$= C^4 H^5 O, 2SO^3 + C^4 H^5 O, HO, 2SO^3 + 2(C^4 H^5 O, HO).$$

Proc. of Amer. Phil. Soc., No. 41.

On the Amount of Ammonia contained in the Atmosphere. *By* M. Fresenius.

The presence of small quantities of ammonia in the atmosphere has been placed beyond doubt by the experiments of Scheele, De Saussure, Colard de Martigny, Faraday, W. Zimmermann, Brandes, Chevalier and Liebig. Nevertheless science as yet possesses but very uncertain data relatively to the proportions in which this alkali is mixed with the atmosphere. To be satisfied of this, it suffices to compare the results of two analyses made on this subject by M. Gräger* and Dr. G. Kemp†. The first sought to determine the quantity of ammonia contained in the atmosphere by passing 1·112 cubic metres of air through weak hydrochloric acid, evaporating the acid liquid after the addition of some bichloride of platinum, and weighing the residue of ammonio-chloride of platinum after suitable washing with alcohol containing æther. He found by this process 1,000,000 grms. of air to contain 0·323 grm. of ammonia =0·938 carbonate of ammonia.

This determination is probably not free from error, M. Gräger having neglected to determine the quantity of ammonia which might

* Chem. Gaz., vol. iv. p. 34. † *Ibid.*, vol. vi. p. 99.

be contained in the reagents themselves. The same must be said of the determination made by Dr. Kemp, by passing through a solution of corrosive sublimate air collected 300 feet above the Irish Sea. When the experiment was finished, the mercurial solution was boiled, and the white precipitate obtained, to which Dr. Kemp assigns the formula ($HgCl+2HgO+HgNH^2$), was weighed. According to this experiment, 1,000,000 grms. of air contain 3·68 grms. of ammonia = 10·37 grms. carbonate of ammonia, *i. e.* eleven times the quantity stated by M. Gräger. The question is evidently far from being solved by these experiments; it however deserves a very careful investigation, on account of the very important part ascribed to atmospheric ammonia in vegetation. These considerations induced the author to undertake some experiments on the subject, which were made in the following manner:—To aspire the air the author employed two large gasometers, each capable of containing 10,000 cubic centimetres; they were in action alternately day and night. The air which they aspired was received through a long tube above the house of M. Fresenius at Wiesbaden, which is situated on an elevation at one extremity of the town. The air, before entering the gasometer, had to pass through a small condensing apparatus, formed of two small balloons connected with each other and filled with dilute hydrochloric acid. The acid was prepared by mixing 1 part of pure acid of 1·12 spec. grav. and 20 parts water. Every morning during forty days one of these condensing apparatus was set in communication with a gasometer filled with water, which in the course of the day flowed into the other empty gasometer. This worked in its turn during the night with another condensing apparatus, and emptied itself into the first gasometer. In this manner the quantities of ammonia contained in the air, both during the day and during the night, were collected separately. In the month of August 1848, 218,650 cubic centimetres traversed one of the apparatus during the day, and 217,050 cubic centimetres passed through the other apparatus during the night. During the month of September, 126,600 cubic centimetres of air passed through during the day, and 127,200 during the night.

When this operation was concluded, the contents of each condensing apparatus were poured into a porcelain capsule, care being taken to rinse the apparatus with a sufficient quantity of distilled water. The contents of the capsule, mixed with 4 grms. of a dilute solution of chloride of platinum, were evaporated to dryness on the water-bath. The residue was exhausted with a mixture of 2 vols. concentrated alcohol and 1 vol. of æther, which removed the excess of chloride of platinum. There remained after this treatment a minute quantity of ammonio-chloride of platinum, which was collected and washed with a mixture of alcohol and æther upon a small filter of Swedish paper, the weight of which had been carefully determined; the salt was then decomposed by heat, the filter incinerated, and the residue, consisting of metallic platinum and the ash of the filter, weighed. At the same time the amount of ammonia contained in the reagents, in the hydrochloric acid, water and chlo-

ride of platinum, was carefully determined. Care was taken to use exactly the same quantities as had been taken for the experiments. The filtering paper left 0·0011 ash for 0·2487 grm. of paper.

The following are the numbers given by M. Fresenius:—

a. The reagents furnished—

Platinum and ash	0·00270
The filter weighed 0·2004, and should have yielded ash	0·00088
Platinum =	0·00182

b. The air which passed during the day gave—

Platinum and ash	0·00270
Ash	0·00064
Platinum =	0·00206

c. The air which passed during the night gave—

Platinum and ash	0·00290
Ash	0·00067
Platinum =	0·00223

Now if we deduct the amount of platinum found in *a* from those found in *b* and *c*, we have—

For *b*	0·00024 platinum.
For *c*	0·00041 ...

according to which 1,000,000 grms. of air contain during the day 0·098 grm. of ammonia = 0·283 carbonate of ammonia. During the night the same amount of air contains 0·169 ammonia = 0·474 carbonate of ammonia.

These experiments have but one fault—the quantity of ammonio-chloride of platinum collected is much too small. A slight error in the weighing, or in the determination of the ash, or a minute loss, might exert an enormous influence on the results. The author therefore considers that it is requisite to undertake further experiments on the subject upon a larger scale; in the mean time the preceding data may serve as an approximation.—*Journ. de Pharm. et de Chim.*, April 1849.

On a new Alkaloid contained in the Seed of Agrostemma Githago.

By H. Schulze.

This alkaloid, which the author has called *agrostemmine*, is contained most abundantly in the outer coat of the seed. The entire seeds were exhausted with weak alcohol to which some acetic acid had been added, the concentrated liquid mixed with magnesia, and the dried precipitate treated with alcohol. On evaporating this solution, the alkaloid separated in crystals, which after frequent recrystallization formed yellowish-white laminæ. They fuse at a slightly elevated temperature, dissolve with difficulty in water, readily in

alcohol, communicating to it an alkaline reaction. It furnishes, by neutralization with dilute acids, crystalline salts. The platinum double salt was obtained as a reddish-brown crystalline precipitate, by mixing an alcoholic solution of agrostemmine with chloride of platinum. The chloride of agrostemmine and gold separates slowly in yellow granular crystals from an alcoholic solution.

The sulphate is obtained in beautiful crystals, which are readily soluble in hot water, still more so in alcohol. The phosphate forms a bulky precipitate.

On boiling with solution of caustic potash, it is decomposed with evolution of ammonia, differing in this respect from all the other natural alkaloids. The solution then furnishes a white precipitate with muriatic acid. Concentrated sulphuric acid colours it first red, and then blackens it.—*Archiv der Pharm.*, lv. p. 298; lvi. p. 163.

Production of Sugar in the Urine by wounding the Brain.

On the 26th of March 1849, M. Magendie announced to the French Academy a very important and entirely unexpected discovery made very recently by M. Bernard. He has found that by wounding a certain part of the floor of the fourth ventricle, the composition of the urine becomes altered, and sugar makes its appearance in it.

The puncture is made by passing the instrument through the inferior orifice of the ventricle, and soon afterwards the urine of the animal (a rabbit), which before the operation is turbid, alkaline and free from saccharine matter, becomes abundant, clear, and contains in solution a very large quantity of sugar, and resembles that of diabetes. In general not more than an hour and a half or two hours are requisite for the complete production of this change in the characters of the urine. The blood also contains a large amount of sugar.

The experiments have hitherto been made upon sixteen rabbits; and by varying them, M. Bernard has found that the point of the fourth ventricle which must be wounded to produce this remarkable phænomenon of the appearance of sugar in the blood and urine was very limited, and corresponded to a space situated a little above the origin of the eighth pair of nerves.

These results, which are so surprising from their novelty, cannot at present be in any way explained. They merely serve to show the remarkable influence which the nervous system exerts upon the functions of nutrition; and in this light they deserve the serious attention of chemists.

The experiments, which have also brought to light some other interesting particulars, are being continued upon animals of different kinds and placed under various circumstances. M. Bernard hopes soon to be able to lay the results before the Academy.

ANALYTICAL CHEMISTRY.

On the Estimation of Phosphoric Acid and on its Separation from Bases. *By* HENRY ROSE.

[Continued from p. 187.]

Separation of Phosphoric Acid from its Combinations by means of Sulphuric Acid and Alcohol.

No method appeared to me more suitable, in the examination of a mixture of phosphates, for separating the phosphoric acid from the bases, than decomposing the phosphates by sulphuric acid and separating the bases combined with sulphuric acid by means of alcohol from the free phosphoric acid. All the sulphates which contain powerful bases are insoluble in strong alcohol; and only those with weak bases, such as peroxide of iron and alumina, are soluble in it, and even these but very sparingly. This method has long been employed with considerable advantage in the analysis of the phosphate of lime. It is true the sulphate of lime is insoluble even in weak alcohol, and can therefore be entirely separated; but whether other phosphates could be decomposed in a similar manner had first to be ascertained by experiment. These were made upon phosphate of magnesia, phosphate of soda and pyrophosphate of soda. [As the results of the experiments were decidedly unfavourable, we omit the details; Professor Rose observes that "it is perfectly evident from these experiments that the complete separation of phosphoric acid from strong bases cannot be effected by sulphuric acid and alcohol even with the addition of a considerable amount of æther."]

In order to separate phosphoric acid from alumina, Rammelsberg decomposes the compound with sulphuric acid, adds sulphate of potash, and separates the alum from the free phosphoric acid by means of alcohol. I have tried this method, substituting sulphate of ammonia for the sulphate of potash, in order, when alkalies are present, to obtain these also separated from the phosphoric acid.

Experiments were made on phosphate of alumina, when 48·93 per cent. was obtained instead of 41·84 alumina. Phosphate of iron was then tried; but instead of 52·31 per cent., 55·18 per cent. of peroxide of iron was obtained, which, dissolved in muriatic acid, mixed with tartaric acid and sulphate of magnesia and chloride of ammonium, gave a considerable precipitate of ammonio-phosphate of magnesia on supersaturating with ammonia. In a second slightly modified experiment, a less amount of peroxide of iron than was required by theory was obtained; but even that was not free from phosphoric acid. Neither the phosphate of alumina nor the phosphate of iron can be accurately separated according to the above method. But since the sulphate of potash and the sulphate of ammonia form a series of double salts with several other sulphates, which might perhaps resist more completely the solvent action of the alcohol than the latter alone, an attempt was made to decompose the phosphate

of magnesia according to this plan. But here only 39·37 per cent. of phosphoric acid were obtained instead of 63·36; the enormous loss was owing to the phosphoric acid having escaped with the vapours of the sulphuric acid. As however in this experiment the amount of magnesia was obtained with tolerable accuracy, the experiment was repeated. 1·578 grm. phosphate of magnesia was heated with concentrated sulphuric acid at a very gentle heat; an equal amount of sulphate of ammonia then added, and again heated very gently until the mass formed a clear liquid, which formed on cooling a thick syrup. This was dissolved in the smallest possible amount of water at a gentle heat, and the clear liquid poured into a large amount of alcohol of 0·833. After the precipitate had subsided, æther produced only a very slight turbidness in the clear liquid. After standing twelve hours, it was collected on a filter, and washed with a mixture of æther and alcohol. This time it dissolved wholly in water, and the solution did not exhibit the slightest turbidness on the addition of chloride of ammonium and ammonia. On precipitation by phosphate of soda, 1·587 grm. calcined phosphate of magnesia was obtained, which is a trifle above the amount of salt used. It is possible therefore to separate magnesia from its combination with phosphoric acid, and to determine its amount accurately by means of sulphuric acid and the assistance of sulphate of ammonia, æther and alcohol. But it is not possible to separate alumina and peroxide of iron according to this plan. It must also be observed, that the insoluble residue, consisting of sulphate of magnesia and sulphate of ammonia, must be washed for a very long time with alcohol containing æther, in fact until a few drops of the liquid evaporated on platinum foil do not leave a black ring, disappearing on ignition, which arises from phosphoric acid, the blackening being produced by the action of this acid upon alcohol at an elevated temperature. If this precaution is neglected, the aqueous solution of the residue, insoluble in alcohol, furnishes with chloride of ammonium and ammonia a more or less considerable precipitate or opacity.

But with every precaution the amount of phosphoric acid cannot be determined with accuracy according to this method; for on applying the most gentle heat to the mixture of phosphate of magnesia and sulphuric acid, some phosphoric acid is always volatilized. On diluting the alcoholic liquid with a large amount of water, adding sulphate of magnesia, chloride of ammonium and ammonia, only 56·71 instead of 63·36 per cent. of calcined phosphate of magnesia were obtained.

As the separation of magnesia from phosphoric acid succeeded by this method, it was tried for the decomposition of the phosphate of soda; the result however was decidedly unfavourable, only 88·21 per cent. being obtained.

All the experiments described prove satisfactorily that it is impossible to obtain the object sought for, that of separating all the bases completely from phosphoric acid, by decomposition with sulphuric acid and alcohol.

An experiment was now made to estimate the acid and bases in a mixture of phosphates by the combination of several methods.

0·348 grm. perphosphate of iron ($Fe^2 O^3 PO^5$), 0·259 grm. phosphate of magnesia ($2MgO, PO^5$), and 0·386 grm. phosphate of lime ($2CaO, PO^5$), were first fused with carbonate of soda, the fused mass treated with water, the insoluble residue collected on a filter, the filtered liquid supersaturated with hydrochloric acid, and the phosphoric acid then precipitated by sulphate of magnesia, chloride of ammonium and ammonia. 0·689 grm. calcined phosphate of magnesia was obtained. The insoluble residue was dissolved in hydrochloric acid, the solution mixed with tartaric acid and supersaturated with ammonia; a precipitate resulted, which was collected on a filter, washed and decomposed with concentrated sulphuric acid; sulphate of ammonia was then added to it, and the whole gently heated. The cold residue was dissolved in as little water as possible and poured into alcohol. The precipitate, washed with alcohol, was dissolved in water, and the solution mixed with ammonia and oxalate of potash; but no oxalate of lime was precipitated, and only a trace of peroxide of iron, which was collected on a filter. Phosphate of soda produced in the filtered liquid a precipitate of phosphate of magnesia, which after calcination weighed 0·082.

The alcoholic liquid was then mixed with a considerable quantity of water, and exposed to a gentle heat until the alcoholic odour was no longer perceptible; it was then mixed with sulphate of magnesia, chloride of ammonium and ammonia, when 0·190 grm. of calcined phosphate of magnesia was obtained.

The liquid containing the peroxide of iron dissolved in the tartaric acid was evaporated to dryness, the dry mass heated to redness, and the cinder burnt as much as possible with access of air. The residue was treated with hydrochloric acid, the solution filtered and precipitated with ammonia; 0·161 grm. peroxide of iron was obtained.

The filtered liquid was mixed with oxalate of potash, and oxalate of lime precipitated, which, converted into carbonate, contained according to theory 0·159 grm. pure lime.

The liquid separated from the oxalate of lime furnished with phosphate of soda 0·163 grm. calcined phosphate of magnesia.

If we calculate the quantities of the bases and of the phosphoric acid in the phosphates employed, and compare them with those found, we obtain the following results:—

	Calculated.	Found.
Phosphoric acid	54·58	56·18
Peroxide of iron	18·13	16·31
Magnesia	9·56	8·95
Lime	17·33	16·01
	100·00	97·45

The results of this analysis have been communicated merely to show, that notwithstanding the utmost care, only a somewhat approximate result was obtained by this long and tedious method.

Separation of Phosphoric Acid from Bases by means of Nitric Acid and Metallic Mercury.

After all the methods above described had failed in separating phosphoric acid from all bases by a single operation, and even complicated methods had furnished very unsatisfactory results, I succeeded, after many fruitless experiments, in discovering a method which furnishes a result as accurate as it is quick. It is as follows:—The phosphatic compound or the mixture of phosphates is dissolved in nitric acid. Neither too small nor too large an amount of acid should be employed. The acid solution is then conveyed into a small porcelain dish, but not too small, so that no loss may occur from ejection; and so much metallic mercury then added, that at least a small portion is left undissolved by the free acid. Upon this the whole is evaporated in a water-bath to perfect dryness. If the dry mass while warm still smells of nitric acid, this cannot be wholly removed by heating further in the water-bath, which however is essentially requisite for the success of the operation. In this case water is added to the dry mass, and the whole again evaporated in the water-bath to perfect dryness. It is frequently advisable to repeat this treatment until the dry mass no longer smells of nitric acid while warm. It is not necessary to add more water than just enough to moisten the dry mass. Cold or hot water is now added, and the whole filtered through a very small filter; the residue washed with cold or hot water until a few drops of the filtered liquid evaporated upon platinum leave no residue on ignition. In general a very considerable residue is left on evaporation, consisting of protonitrate of mercury; but this entirely disappears on ignition.

The filtered liquid contains all the bases which had been combined with the phosphoric acid united with nitric acid, along with a considerable quantity of protonitrate of mercury and some pernitrate; hydrochloric acid is added to it. If the precipitate it produces is very considerable, it is collected upon a filter and washed. On ignition the protochloride of mercury leaves no residue; if, on the other hand, the precipitate is but small, ammonia may be added immediately to the liquid; there is then formed a black precipitate, and a white one consisting of perchloride of mercury and amidogen. However, this method can only be applied when there are no bases present which are precipitated by ammonia. The precipitate frequently contains some peroxide of iron. The precipitate must be quickly filtered and washed, protected from access of air, in order that no carbonate of lime may separate if this base be present. When magnesia is present, it is advisable to add some chloride of ammonium to the liquid, to prevent its being precipitated by the ammonia. If the decomposition has been perfectly effected, the precipitate produced by ammonia, which is frequently very considerable, leaves on ignition only a few milligrammes of peroxide of iron; but sometimes a considerable residue, amounting to several decigrammes, is left. In that case the decomposition has not been complete, or the whole of the free nitric acid not expelled. It is also possible that

too little nitric acid was employed to dissolve the phosphatic compounds, so that there was not sufficient protoxide of mercury formed to separate entirely the phosphoric acid. This residue usually consists of phosphate of magnesia and peroxide of iron.

In all cases it is advisable not to throw away the washed mercurial precipitate, but to calcine it after desiccation, in order to submit the residue to examination. If it consist of earthy phosphates, the treatment with mercury and nitric acid must be repeated. If it consist solely of carbonate of lime or of magnesia, it is only requisite to dissolve it in hydrochloric acid, and to add it to the liquid separated from the precipitate produced by ammonia. As sometimes earthy phosphates may be contained in the precipitate, oxalic acid must not be added immediately after the precipitation by ammonia, for the purpose of throwing down the lime.

It is unnecessary to observe that the precipitate should be heated to redness under a chimney with a strong draught, that no injury may arise from the mercurial vapours.

The alkalies, lime, magnesia, and other metallic oxides contained in the liquid filtered from the precipitate, are separated by the usual methods.

The mercury may likewise be removed from the solution of the nitrates by evaporating the solution in a platinum dish, and exposing the residue to a red heat in a platinum crucible. In many cases this method is more simple and advantageous. The large amount of ammoniacal salts introduced in order to remove the mercury, the expulsion of which is connected with much inconvenience, is avoided. It should however be observed, that when alkaline nitrates are present, the dry residue on ignition must be mixed with a small quantity of dry carbonate of ammonia, in order to convert into carbonates the free alkalies produced by the decomposition of the nitrates. If this precaution is neglected, the platinum crucible is very much acted upon. The calcined residue is dissolved in dilute hydrochloric acid, and the bases separated in the usual manner.

We now come to the determination of the phosphoric acid in the residue insoluble in water. This contains protophosphate of mercury, protonitrate and metallic mercury. A certain amount of persalt has been formed from the protosalt by the treatment with water; and if the washing has been long continued with hot water, merely oxide is obtained.

The following method of determining the phosphoric acid in this residue has been found from long experience to be the best. The filter with the mercurial salts is well dried; the latter shaken from the filter into a platinum crucible, and mixed with an excess of carbonate of soda, or what is better, a mixture of carbonate of potash and carbonate of soda, as a less heat is then required to fuse the mass. A little hollow is now made in the mixture; the filter rolled up into a little ball and placed in the hollow, covered with the mixture, and over the whole is spread a layer of carbonate of soda. The crucible is then exposed for about half an hour under a chimney with a good draught to a moderate but not red heat, that the

contents may not fuse. At this temperature the whole of the metallic mercury and the mercurial salts with the exception of the protophosphate are expelled. The strongest heat to be obtained with an Argand lamp and strong spirit is now applied; there is no need to fear any boiling over, as the mass has considerably diminished in bulk by the first heating. The fused mass is treated with hot water, in which it dissolves entirely if the operation has been conducted with care and no iron was contained in the compound. It is supersaturated with hydrochloric acid, and then sulphate of magnesia, chloride of ammonium and ammonia added to precipitate the phosphoric acid in the usual manner.

The above plan should be carefully adhered to in heating the mixture of the mercurial salts with the alkaline carbonates, otherwise a false result is frequently obtained; for instance, if the filter and its contents were not perfectly dry before being mixed with the dry alkaline carbonates, or if too great a heat was applied at the commencement, the mass froths very considerably; whilst when the mixture is perfectly dry, the protonitrate of mercury is expelled at a gentle heat, without acting upon the carbonate of soda. Moisture and a strong heat produce decomposition with violent effervescence; the nitrate of soda produced is decomposed at a higher temperature, and acts violently on the platinum crucible; oxide of platinum is formed, and the crucible is found to have decreased some centigrammes, and frequently even some decigrammes in weight. A brown powder is left on solution in water, which dissolves very sparingly in muriatic acid. It is washed with pure water, when no oxide of iron is contained in the substance examined.

When mercurial salts are heated alone in the platinum crucible without being mixed with carbonated alkali, there remains after the ignition a glass of phosphoric acid, which curiously enough always retains some mercury, even when the crucible has been exposed to a very intense heat.

The following precautions should not be neglected. So much metallic mercury should be added to the solution of the substance in nitric acid, that a tolerable quantity of globules of mercury are distinctly perceptible in the dry mass. If this is not the case, mercury and water should be added, and the whole again evaporated in the water-bath. It is essentially requisite to the success of the experiment that the evaporation should be made on a water-bath; for if the temperature should have exceeded that of boiling water, even for a very short time, a certain amount of the nitrates may have been decomposed and some nitric acid been lost. The basic nitrate of mercury or the oxide will then be left undissolved along with the protophosphate of mercury in the treatment with water. But none of the nitrates with strong bases are decomposed at the temperature of boiling water.

All the compounds of phosphoric acid can be so perfectly decomposed by this method, that on the one hand we obtain the bases free from every trace of phosphoric acid, and on the other the phosphoric acid free from any traces of the bases with which it had been com-

bined, which is not possible by any other method. All bases form with nitric acid soluble neutral salts, and can consequently be completely separated by water from the insoluble protophosphate of mercury.

When weak bases are present, the treatment must be slightly modified. This refers especially to the phosphate of iron and phosphate of alumina. The combinations of these bases with nitric acid cannot be evaporated in the water-bath without parting with a portion of their acid, and become for the greater part insoluble in water. Iron very frequently occurs in the ashes of organic substances; but it is remarkable that hitherto alumina has not been detected in them, at least not with certainty. The modification which the presence of iron requires is not considerable; but the presence of alumina renders the method far more complicated.

When phosphates containing iron are evaporated as described with nitric acid and mercury, the greater portion of the peroxide of iron is left on treating the dry residue with water with the protophosphate of mercury, and only a small portion dissolves with the nitrates; it is filtered and washed in the usual way, the peroxide of iron in the solution determined with the other bases, and the insoluble portion fused with carbonate of soda. On treating the fused mass with water, the peroxide of iron is obtained perfectly free from phosphoric acid, whilst the entire amount of phosphoric acid in combination with soda is dissolved.

When the fusion with carbonate of soda has been effected with the precautions above-described, the peroxide of iron dissolves in muriatic acid without any residue, and can be precipitated from the solution by ammonia. Sometimes, however, when too great a heat has been employed at the commencement, a reddish-brown powder is left, which even after long digestion in hydrochloric acid remains undissolved, and consists of oxide of platinum. A small portion however dissolves with the peroxide of iron in the acid. Notwithstanding the presence of platinum, the iron may be accurately precipitated by ammonia without the precipitate containing any platinum, only it is requisite to employ a somewhat large amount of ammonia; the precipitate then is of a pure reddish dark brown colour, and the ammonio-chloride of platinum is dissolved in the excess of ammonia. The liquid filtered from the iron is colourless, and gives with sulphuret of ammonium a blood-red precipitate soluble in a large excess of the precipitant.

When phosphate of alumina is present, the investigation becomes more complicated. Although the phosphoric acid can be perfectly separated by nitric acid and mercury, the nitrate of alumina is decomposed like the nitrate of iron by the heat of the water-bath, only less easily. 1·030 grm. phosphate of alumina, $Al^2 O^3 PO^5$, was treated with nitric acid and mercury, and the dry residue exhausted with water; the liquid passed turbid through the filter, which is not the case with iron; it was therefore filtered again, and the amount of alumina determined in it. Only 0·272 grm., or 26·40 per cent., was obtained instead of 41·84.

Since the phosphate of alumina cannot be decomposed by fusion with carbonate of soda, silicic acid must be added on fusion, and the separation effected in the usual manner. Excepting the phosphate of alumina, all the other phosphates, at least those which occur most frequently, can be decomposed more readily and completely than is possible by any other method. I have not enumerated any analyses to support this assertion; but during three years, since I introduced this method in my laboratory, a very large number of compounds of phosphoric acid, especially such as are contained in the ashes of organic substances, have been examined by me, by M. Weber, and by several other young chemists, with the most favourable results.

I have on that account not made further experiments on some other methods which have been proposed for the decomposition of phosphatic compounds, and especially on that of Schulze, for separating the compounds of phosphoric acid with peroxide of iron, alumina and lead from other phosphates by acetic acid, since this method requires great precaution in using it, and frequently leads to incorrect results.

After I had written this paper I became acquainted with Fresenius's experiments on the same subject*. I am therefore not able to enter into a minute criticism of his method; I must however observe, that his experience is in contradiction to mine as to the phosphate of iron not being completely decomposed by fusion with carbonated alkali. Not only earlier, but even very recent experiments made in my laboratory, besides those mentioned in this paper, have demonstrated that the decomposition is complete.—Poggendorff's *Annalen*, March 1849

Testing Butter for Caseine.

A simple method of detecting the caseine still contained in butter is to shake a weighed quantity in a flask with æther, when the butter dissolves in the æther, leaving behind the caseine.—*Archiv der Pharm.*, lvi. p. 327.

PATENTS.

Patent granted to William Longmaid, *for Improvements in treating the Oxides of Iron, and in obtaining Products therefrom.*

This invention consists in certain modes of treating the oxides of iron, for the purpose of obtaining a black or dark coloured pigment, or a volatile oleaginous product, and an inflammable gas.

The oxide of iron is finely pulverized, and then mixed intimately

* Chem. Gaz., p. 18 of the present volume.

with some carbonaceous matters. The proportions vary considerably. The addition of 10 per cent. of carbonaceous matters would generally be sufficient; but the patentee prefers to use a little excess of carbonaceous matters; and therefore he mixes the oxide of iron with from 12 to 15 per cent. of carbonaceous matters, or such a quantity, that when the process is complete, a slight excess of carbonaceous matter will remain in the retort employed. Any kind of carbonaceous matters, which are not too volatile or expensive, and which can be mixed intimately with the oxide of iron, may be used; but when not in a fluid state, they must be pulverized. Those preferred by the patentee are resin and tar. When resin is used, it must be pulverized, and the oxide of iron mixed therewith in a dry state. When tar is employed, the oxide of iron is mixed therewith in a moist state, for the purpose of facilitating the incorporation of the materials; and the mixture is dried at a temperature sufficiently high to deprive it of nearly the whole of its moisture, and reduce it to a state of powder.

The mixture is to be put into retorts or close vessels; and the patentee prefers to use cast iron retorts of the ordinary kind, 5 feet in length and 1 foot in diameter, with a cover to be fastened on the open end, and a ring at the opposite end for the purpose of lifting it. A retort of this size may be charged with $1\frac{1}{2}$ cwt. of the mixture; and then (the cover being secured) it is lifted by a crane, and placed in a suitable furnace, in a vertical position, with the cover end downwards, in order that the volatile products evolved from the mixture may be consumed, and thus aid in heating the retort. The heat is to be gradually raised until the whole of the retort has arrived at a low red heat; at which temperature it must be kept until about two hours after the evolution of the combustible volatile products has ceased; and then, the process being complete, the retort is removed from the furnace, and allowed to become cold, or nearly so, before the charge is withdrawn, as it would be injured by contact with the air whilst hot. The material produced will be black or dark coloured, and will form a good pigment for many purposes. Some carbonaceous matters, when used in the production of this material, will cause it to be sufficiently pulverulent; but when this is not the case it must be ground or pulverized. The pulverized matter is to be ground with oil, so as to form paint, in the usual way.

When the patentee does not intend to burn the combustible volatile products of the calcination, he lutes the cover on to the retort, so as to make it air-tight, and inserts a pipe therein to convey the volatile products to a condenser. The calcination will cause a volatile oil to be evolved from the contents of the retort, and the oil will pass through the pipe into the condenser, where it will be condensed. The calcination will also cause the evolution of an inflammable gas, suitable for the purposes of illumination; which gas must be conveyed by a pipe from the condenser to a gasometer.—Sealed Oct. 26, 1848.

Patent granted to Thomas Richardson, Newcastle-on-Tyne, *for Improvements in the Condensation of Metallic Fumes, and in the Manufacture of White Lead.*

This invention comprises two divisions:—

1. *Improvements in the Manufacture of White Lead.*—Lead of that character known in commerce as tea lead is to be submitted in a melted state to a slow current of heated air in an ordinary red lead furnace, or in the iron pan employed for calcining hard lead, by which means the tin contained therein will be caused to separate from it and float upon the surface, together with a variable quantity of the oxide of lead, which is to be removed with an iron rake. The completion of this part of the process is known by the lead becoming so soft that it may be scratched with the finger, when the remaining materials are to be taken away also. The lead is then to be reduced into crystals by the desilverizing process of Mr. Pattinson, or employed in a granular state. The prepared lead is to be moistened by the application of certain proportions of nitric or acetic acid of commerce, or nitrate or acetate of lead, diluted with water until of equivalent strength, and the moistened mass turned over from time to time; and when sufficiently treated in this manner, about 20 to 30 cwt. of the same is to be placed in chambers lined with lead, slate or stone, the latter being preferred, fitted into a suitable frame, provided with doors, and having spaces between each of such chambers, into which spaces heated air is to be admitted (by means of a pipe furnished with a stop-cock), in order to keep the chambers at a proper temperature. Carbonic acid gas is to be introduced into the chambers with the prepared lead by means of pipes with stop-cocks; the heat is to be kept up, and steam admitted occasionally. At the expiration of from ten to fourteen days the materials will be properly treated, when they are to be removed from the apparatus, ground between a pair of stones, and washed in a dolly-tub, which separates the metallic lead from the white lead, the former being returned with a fresh supply to the chambers.

2. *Improvements in the Condensation of Metallic Fumes,* which consist in introducing steam into the main pipe connecting the furnaces, by means of a small iron pipe situate at a distance of 2 feet or 3 feet beyond the furnace, and in building near the chimney a tower not less than 20 feet high, divided internally by a partition wall which reaches nearly to the top thereof; iron bars are placed across, upon which a layer of coke or pieces of broken brick is placed. The fumes ascend up the one compartment, but are intercepted in their passage down the other by the layer of coke or broken brick, upon which water flows in from the top. If the draught be not sufficient to draw through the coke, it must be increased by means of steam jets.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Behaviour of Iron and Zinc towards Sulphuric Acid and its Compounds. By ALBERT D'HEUREUSE.

THE behaviour of anhydrous sulphuric acid and of the sulphates towards iron and other metals at a red heat had never been accurately investigated; it was known that they reacted on each other, and formed various products, which however had been but very imperfectly studied. The author has published his experiments on this subject in a very extensive memoir, from which we take the following.

Anhydrous Sulphurous Acid with Iron or Zinc.—No reaction takes place at the ordinary temperature; at a red heat a thin iron wire, in contact with anhydrous sulphuric acid, becomes coated with a black stratum, consisting of a mixture of peroxide of iron with sulphuret of iron. A more perfect decomposition was obtained by placing in a spacious porcelain crucible a smaller one containing short pieces of thin iron wire; the whole was placed in a crucible with sulphate of bismuth, closed with a lid, and a mixture of clay and oxide of lead, which forms a very infusible glass on ignition. After exposure for half an hour to a red heat in a blast-furnace, the iron had become converted into a vesiculous fused mass of a metallic-green colour, partially yellowish or beautiful dark blue upon the surface, and with the fracture of a bronze colour. When reduced to a fine powder, it dissolved, but with difficulty and imperfectly, in cold muriatic acid with a yellow colour; on the application of heat, sulphuretted hydrogen was disengaged. To ascertain the decomposition that had taken place, the iron and the product obtained by the action of the anhydrous sulphuric acid were weighed; and lastly, the amount of sulphur determined in the latter. It was found that the decomposition should be expressed by the equation—

$$4SO^3+13Fe=3(FeO,Fe^2O^3)+4FeS.$$

A small portion of the sulphuric acid must however be decomposed at a strong red heat into oxygen and sulphurous acid, since the amount of sulphur found does not exactly correspond with the above decomposition.

When zinc is treated in a similar manner, a greenish-yellow powder, consisting of oxide and sulphuret of zinc, is obtained—

$$SO^3+4Zn=3ZnO+ZnS.$$

Alkaline Sulphates with Zinc and Iron.—Sulphate of potash is entirely decomposed after exposure for a short time to a red heat with finely-divided iron. The blackish porous mass contains no sulphuret of potassium, but sulphuret of iron and caustic potash.

A direct analysis of the product could not be made. On this account the sulphuric acid remaining on ignition with an excess of sulphate of potash was determined; and it was found that 1 atom of sulphuric acid required 3 atoms of iron for its decomposition. The reaction takes place consequently according to the following formula:—

$$KO, SO^3 + 3Fe = KO + Fe^2O^3 + FeS.$$

Although the decomposition of the sulphuric acid in the presence of an excess of iron is complete, this reaction cannot be used for the preparation of potash free from sulphur; because, on solution in water, a portion of the sulphuret of iron dissolves with a green colour, which disappears, it is true, with the access of air, but with the production of sulphuret of potassium and hyposulphite of potash.

An addition of copper prevents the solution of the sulphuret of iron; but even in this case the potash contains some hyposulphite. Impure carbonate of potash however can be entirely deprived of sulphur by fusion with iron.

When excess of zinc is heated to redness with sulphate of potash, a compact mass of a lemon colour is obtained, which consists of sulphuret of potassium and oxide of zinc—

$$KO, SO^3 + 4Zn = KS + 4ZnO.$$

On heating to redness a mixture of sulphate of potash with not too small a quantity of zinc, a remarkably beautiful deflagration takes place, which begins at a faint red heat at one point of the margin, and rises to a white heat, when a portion of the zinc burns with a dazzling light.

Sulphate of Soda behaves towards iron almost exactly like the potash salt, only more sulphuret of iron is dissolved upon the addition of water. It likewise exhibits the same behaviour towards zinc.

Sulphate of Ammonia.—On boiling a solution of this salt with iron, ammonia escapes, and the solution contains a protosalt of iron. If the mixture is fused at a gentle heat, the disengagement of ammonia is still stronger, and the colour of the salt becomes darker and greenish on solution in water. On quickly applying a red heat to this mixture, sulphurous acid escapes along with the vapours of the salt, and the surface of the iron becomes coated with oxide and sometimes with sulphuret. This decomposition however does not appear to be direct, but to proceed from the protosulphate of iron produced in the fusion.

Zinc exhibits the same phænomena as iron.

Sulphate of Lime furnishes, when heated to redness with iron in a porcelain crucible, a grayish-black mass of metallic appearance, which contains sulphuret of calcium and an oxide of iron. By determining the amount of sulphuric acid which a known weight of

iron decomposes, it was found that the following two decompositions must have occurred:—

$$CaO, SO^3 + 3Fe = CaS + FeO, Fe^2 O^3$$

and

$$3CaO, SO^3 + 8Fe = 3CaS + 4Fe^2 O^3.$$

Pure zinc furnishes, on being ignited with sulphate of lime, a yellowish imperfectly fused mass, which contains no sulphuret of calcium—

$$CaO, SO^3 + 4Zn = CaO + 3ZnO + ZnS.$$

On heating a mixture of *sulphate of baryta* and iron to redness, a semi-fused metallic mass is obtained, which contains sulphuret of barium and oxide of iron. On comparing the quantities of the iron consumed and of the sulphate of baryta decomposed, it was found that the following two reactions must have taken place:—

$$BaO, SO^3 + 3Fe = BaS + FeO, Fe^2 O^3.$$

$$3BaO, SO^3 + 8Fe = BaS + 4Fe^2 O^3.$$

The decomposition of the sulphate of baryta is much more readily effected by iron than by coal; but the sulphuret of barium is only imperfectly extracted from the product by long boiling with water. Very good crystallized chloride of barium was obtained by heating to redness 2 parts of heavy spar, 2 parts of iron and 1 part chloride of calcium, reducing the cold mass to a powder, and exhausting with boiling water, and then adding a few drops of muriatic acid. This method of preparing chloride of barium always furnishes excellent results except when too high a temperature has been employed.

Zinc filings furnish, when heated to redness with sulphate of baryta, a compact greenish-yellow mass, which contains no sulphuret of barium—

$$BaO, SO^3 + 4Zn = BaO + 3ZnO + ZnS.$$

The whole of the baryta however cannot be obtained by exhaustion with boiling water, it having entered into a combination with the oxide of zinc, which it is very difficult to decompose by water.

Pure *sulphate of strontia* requires a much higher temperature for its decomposition by iron than the salts of baryta and lime. The powdered mass more readily parts with sulphuret of strontium to water, but by no means with the whole. Chloride of strontium may be prepared from celestine in the same manner as directed under sulphate of baryta.

Zinc behaves towards this salt in the same manner as towards the salt of baryta.

Sulphate of magnesia gives off much sulphurous acid on ignition with iron. A grayish mass is obtained, which exhibits at several spots white magnesia; the iron is converted into oxide, protoxide and some sulphuret.

In these decompositions it is very remarkable that in those cases in which the iron appropriated both the constituents of the sulphuric acid, the zinc combined only with the oxygen; and where

the latter metal had become converted into oxide and sulphuret, the iron remained united with the oxygen.—Poggendorff's *Annalen*, lxxv. p. 255.

On the Products of the Metamorphosis of Lactic Acid by Nascent Chlorine. By Dr. Stædeler.

When lactic acid or a lactate is distilled with chloride of sodium, manganese and sulphuric acid, a product is obtained from which heavy oily drops with the odour of the superchloride of formyle, separate upon the addition of potash.

When there is not sufficient chlorine present, aldehyde is principally formed; potash then merely produces a turbidness in the distillate, and after some time a brown resinous substance (aldehydic resin) separates. This is the case, for instance, when 1 part protolactate of iron, 4 parts of manganese and salt, and 4 parts of sulphuric acid diluted with twice its weight of water, are submitted to distillation. If this relation is varied, so that 10 parts of manganese and salt, 10 parts of sulphuric acid and 12 to 14 parts of water are employed for every one part of the lactate of the protoxide of iron, the action of the chlorine proceeds very regularly; and only in the first portions of the distillate can any aldehyde be detected by the odour and by the reaction with potash. If that which passes over subsequently is collected separately, and rectified over chloride of calcium, the product may be mixed without any evolution of heat or coloration with concentrated sulphuric acid; and when set aside, a colourless liquid, resembling chloral, separates from it. This however is not pure chloral; for on attempting to separate it by distillation from sulphuric acid, the greater portion is decomposed with evolution of hydrochloric acid, and the sulphuric acid becomes coloured black; that which passes over however is principally chloral. With a little water it is converted into crystalline hydrate of chloral; and an addition of potash to the aqueous solution separates superchloride of formyle.

The substance which is destroyed by the hot sulphuric acid appears to be an intermediate product. Its quantity is lessened in proportion as more chlorine is allowed to act upon the lactic acid; and we may suppose that, with a certain proportion of the lactic acid to the chlorine mixture, chloral would constitute the chief product. —Liebig's *Annalen*, March 1849.

On the Atomic Weights of Cerium and Barium. By M. Marignac.

To determine the equivalent of cerium, the author employed the sulphate of the protoxide of cerium, which is easily obtained crystallized and perfectly pure. To procure pure oxide of cerium, the author recommends the following simple method:—Cerite, reduced to a fine powder, is mixed in a porcelain dish with concentrated

sulphuric acid, so as to form a thick paste; on the application of heat a lively reaction occurs; the mass evolves considerable heat, becomes white, and a portion of the sulphuric acid is evaporated, so that in a few minutes nothing but a white dry powder is left. This is transferred into a clay crucible, which is kept for a long time at a temperature below red heat. After cooling, the powder is diffused in cold water, care being taken to add it in small portions at the time, so that no heating may occur, which would cause the powder to cake together. Silica, coloured by some peroxide of iron, is left undissolved; it is separated by filtration. The solutions of the sulphates are for the greater part precipitated by boiling; so that in general it is not worth the trouble to obtain the remainder from the solution. From this precipitate, which contains the sulphates of cerium, lanthanium and didymium, the oxides are prepared according to the usual methods; and these are then separated according to the method described by Mosander. The oxide of cerium is most easy to obtain pure; this, as is well known, remains undissolved on treating the mixed oxides with nitric acid which has been diluted with 100 times its weight of water. It is however requisite to avoid carefully any admixture of sulphuric acid, which is frequently found in the oxides precipitated from the sulphatic solutions by potash or ammonia. The best plan is to dissolve the oxides in nitric acid, and to precipitate the sulphuric acid with a little nitrate of baryta, after which the solution is evaporated to dryness and calcined. When the object is not so much to obtain the whole of the oxide of cerium, as to procure it in as pure a state as possible, it is advisable, after the treatment with dilute nitric acid, to digest the residue with a more concentrated acid, which removes the last traces of didymium and lanthanium along with a small quantity of oxide of cerium. In every case, however, the oxide thus obtained must be redissolved, precipitated with carbonate of ammonia, heated to redness, and again treated with nitric acid. When the oxide of cerium is pure, it becomes almost insoluble in acids after calcination; so that it has to be treated with concentrated sulphuric acid, which readily converts it into sulphate. In this manner a yellow mass of the sulphate of the proto- and peroxide of cerium is obtained, which dissolves readily in water in the presence of a pretty large excess of sulphuric or nitric acid. The yellowish-red solution is set aside to clear; the liquid decanted, and diluted with a large amount of water, which precipitates the greater portion of the dissolved salt in the form of a yellow powder, almost perfectly insoluble in water. Any foreign salt it might contain can easily be removed by washing it with water. By boiling it with sulphuric and nitric acids until it is perfectly decolorized, and evaporating to dryness, it furnishes protosulphate of cerium.

The salt is perfectly colourless, and readily crystallizes on the slow cooling of the solution in rhombic octahedra, the surfaces of which are inclined to the terminal edges in angles of 114° 12′ and 111° 10′. There frequently occurred with these a more acute octahedron with angles of 99° 48′ and 95° 48′.

To obtain it free from any excess of acid, it was dissolved in cold water, and the filtered liquid heated to boiling, when the greater portion of the salt was precipitated. The supernatant liquid was decanted, the precipitate dried, and a portion of it reserved for analysis, but another portion of it treated as above.

As the determination of the equivalent of cerium from this salt depends essentially on that of barium, the author repeated the determination of the latter equivalent according to the process of Pelouze. The chloride of barium for this purpose was purified in the following manner:—

A. Commercial chloride of barium was dissolved in boiling water, and crystallized by cooling.

B. The preceding, strongly calcined, dissolved in boiling water, treated with carbonic acid, filtered and crystallized.

C. The preceding, washed with alcohol and recrystallized.

D. The preceding, after longer washing with alcohol.

The following results were obtained:—

	Silver.	Chloride of barium.	Chloride of barium for 100 parts of silver.	Mean.
A.	3·4445	3·3190	96·356	96·354
	3·7480	3·6110	96·345	
	6·3446	6·1140	96·362	
B.	4·3360	4·1785	96·356	96·354
	4·8390	4·6625	96·352	
C.	6·9200	6·6680	96·358	96·360
	5·6230	5·4185	96·363	
D.	5·8435	5·6300	96·346	96·367
	8·5750	8·2650	96·384	
	4·8225	4·6470	96·361	
	6·8460	6·5980	96·377	

These experiments agree pretty accurately with each other, so that the method undoubtedly merits confidence; however, the variations are greater than in those obtained by a similar method from chloride of potassium, which the author ascribes to the circumstance that the latter can be weighed in fragments, whilst chloride of barium must be dried as a powder in the crucible. It is at the same time evident that for such determinations of the atomic weight the chloride of barium can be perfectly dried at a faint red heat without decomposing it, whilst at a red heat it parts with chlorine and acquires an alkaline reaction. Taking the mean of the two last series of experiments, which were made with the purest salt (96·365 chloride of barium), the equivalent of barium is found to be 856·77 (O=100) or 68·54 (H=1), therefore almost exactly the mean of the numbers found by Berzelius and Pelouze.

The author then proceeded to determine the equivalent of cerium. He first ascertained that the sulphate of the protoxide of cerium may be dried completely, and without decomposition, at a temperature far below red heat. By precipitating with chloride of barium and weighing the precipitate, he obtained—

Sulphate of the protoxide of cerium.	Sulphate of baryta.		Mean.
4·532	5·560 =	122·68 per cent.	
4·172	5·090	122·00 ...	122·40
13·514	16·556	122·51 ...	

The equivalent of cerium deducible from these is 590·2.

This method exhibits two sources of error, which however partly annul each other. On the one hand, the sulphate of baryta always retains traces of oxide of cerium, which cannot be removed by long-continued washing; whilst, on the other hand, sulphate of baryta is soluble to some extent in the presence of salts of cerium. The author therefore resolved to determine the equivalent of cerium by precipitating the protosulphate of cerium with a measured solution containing a known quantity of chloride of barium. For this purpose it suffices to weigh off approximately the quantity of chloride of barium required to precipitate a weighed quantity of protosulphate of cerium, and to complete the precipitation by the addition of a standard solution. However, this method by no means answers so well as in the case of silver. Notwithstanding its weight, the sulphate of baryta separates very slowly, and the liquid must be let stand twenty-four hours after each experiment to obtain it perfectly clear. A portion is then transferred by means of a pipette into a very clear glass, some of the standard solution added, and then set aside for one or two hours to see whether any turbidness results or not; it is then added to the liquid. This circumstance merely influences the duration of the experiment; but the other, *i. e.* the solubility of the sulphate of baryta in salts of cerium, interferes with its accuracy. Whilst in water acidified by sulphuric and muriatic acids an addition of from 4 to 6 milligrammes produces a perceptible troubling, it is requisite to add from 40 to 60 milligrammes to liquids containing salts of cerium for an addition of protosulphate of cerium to produce further turbidness.

Although therefore this process cannot furnish very accurate results, it is nevertheless preferable to the first, because it furnishes at least two limits within which the true equivalent must be included.

The mode of experimenting was as follows:—Both salts were dried one after the other, weighed, and transferred into a bottle containing about 200 grms. of distilled water acidified with muriatic acid. As soon as the liquid had cleared, a little of it was poured into a glass; and by means of a standard solution, 20 milligrammes of chloride of barium added, which produced a troubling. The liquid was returned into the bottle, allowed to deposit, and then a fresh quantity of 20 milligrammes of chloride of barium added; and this repeated as long as any milkiness resulted. The sum of the chloride of barium consumed furnished the lowest limit. The liquid was again returned to the flask, and 40 milligrammes of chloride of barium added, so that on the whole the lowest limit was exceeded by 60 milligrammes. As soon as the liquid had become clear, it was tested by the addition of 18·5 milligrammes protosulphate of cerium (which correspond to 20 milligrammes chloride of barium);

in every case a milkiness resulted, proving the presence of an excess of chloride of barium; the liquid was poured back, and subsequently again mixed with 18·5 milligrammes of the protosulphate; this did not always produce a turbidness, so that the highest limit might be reduced by 20 milligrammes. *A*, *B*, *C*, *D* are the results from the second, third, fourth and fifth crystallizations of the protosulphate of cerium:—

	Protosulphate of cerium.	Chloride of barium. Minimum.	Chloride of barium. Maximum.	Equiv. of protosulphate of cerium. Maximum.	Equiv. of protosulphate of cerium. Minimum.	Equiv. of protosulphate of cerium. Mean.
A.	11·014	11·990	12·050	1196·3	1188·2	1192·2
	13·194	14·365	14·425	1194·0	1189·0	1191·5
B.	13·961	15·225	15·285	1192·0	1187·4	1189·7
	12·627	13·761	13·821	1192·8	1187·7	1190·2
	11·915	12·970	13·030	1194·3	1188·7	1191·3
C.	14·888	16·223	16·283	1193·0	1188·6	1190·8
	14·113	15·383	15·423	1192·7	1189·5	1191·1
D.	13·111	14·270	14·330	1194·4	1189·4	1191·9
	13·970	15·223	15·283	1193·0	1188·3	1190·6

As the salts of the three last crystallizations furnish very nearly the same results, M. Marignac allows the last seven experiments a greater influence upon the mean result. The equivalent of the protosulphate of cerium is accordingly situated between 1193·1 and 1188·5; which last number must necessarily be too small, whilst the first is too great. It is uncertain to which of the two limits the true value is nearest; but no very great error will be committed by adopting the mean of these numbers, or 1190·8. This gives for the equivalent of cerium the number 590·8 (O=100) or 47·26 (H=1). —*Arch. des Sciences Phys. et Nat.*, vol. iii. p. 265.

On the Double Sulphate of the Proto- and Peroxide of Cerium. *By* M. Marignac.

The author analysed this salt, the preparation of which has been described at p. 213, after it had been dried at 212°. The sulphuric acid, cerium and water were determined in the usual manner. The amount of peroxide of cerium contained in it was found by digesting the salt with a known weight of protoxide of iron in muriatic acid, and determining the excess of protoxide of iron with a normal solution of permanganate of potash, by which the amount of oxygen of the oxide could be calculated. The results obtained agree with the following composition:—

Protoxide of cerium	..	..	3 =	26·49
Peroxide of cerium.....	37·05	..	2	37·87
Sulphuric acid.....	26·17	26·09	4	25·57
Water	10·34	10·10	7	10·07

The author determined in the same manner the state of oxidation of the oxide left on calcining the nitrate of cerium. The weight of this residue varies after each calcination, so that it is impossible to

employ it for an accurate quantitative determination. It is almost insoluble in muriatic acid, but dissolves in it when finely powdered in the presence of the protochloride of iron. Three products furnished—

Protoxide of cerium (difference) ..	96·81	96·25	96·17
Excess of oxygen	3·19	3·75	3·83

There is consequently 22·7, 26·9 and 27·5 oxygen in excess for each equivalent of protoxide of cerium; which differs considerably from the composition of a sesquioxide, which should contain more than 50 per cent. oxygen.—*Archiv des Sciences Phys. et Nat.*, viii. p. 278.

On hydrated Valerianate of Zinc. By G. C. Wittstein.

The valerianate of zinc, obtained by precipitating sulphate of zinc with valerianate of soda, or by evaporating the aqueous solution, is anhydrous. If, on the contrary, carbonate of zinc is stirred with so little water as to form a paste, it is converted, upon the addition of the calculated quantity of valerianic acid, into a hydrated salt with 12 atoms of water. This salt, when dried at 122°, perfectly resembles the anhydrous salt. It parts with its water at 212°, and dissolves in 44 parts of water. The solution, on being heated, becomes turbid, but bright again on cooling. When boiled so long that the whole of the sediment does not redissolve on cooling, the residue is the anhydrous salt. The analysis of the hydrated salt dried at 122° furnished—

Oxide of zinc	17·00	1	16·94
Valerianic acid	38·58	1	38·42
Water.....	44·42	12	44·64

Buchner's *Repert.*, i. p. 189.

On Salicylic Æther and some Products derived from it. By A. Cahours.

In my investigation on the heavy oil of *Gaultheria procumbens* (salicylate of methylene), I showed that salicylic æther forms, like the latter, definite crystalline compounds with bases. If the combination of this substance with baryta is submitted to distillation after having been perfectly dried, it furnishes a residue of carbon and a limpid colourless volatile liquid, to which I have given the name of *phenetole*. On analysis it gave the following results:—

Carbon	78·48	16 =	96	78·68
Hydrogen	8·29	10	10	8·10
Oxygen	13·23	2	16	13·13

It is consequently homologous with anisole, $C^{14} H^8 O^2$, from which, in fact, it differs only in the addition of $C^2 H^2$.

I have admitted that anisole might be regarded as the phenate of methylene, founded upon the fact that binitroanisole and trinitroanisole are decomposed by ebullition with an alcoholic solution of potash, into nitrophenesic and nitrophenisic acids. Phenetole may be viewed as the phenic æther of alcohol; in fact, we again meet with the same difference with respect to the boiling-point of these two substances as between the corresponding compounds of methyle and ethyle; anisole boils at 305·6, and phenitole at 341·6.

Phenetole is a colourless extremely mobile liquid, of an agreeable aromatic odour. It is insoluble in water, but dissolves readily in alcohol and æther; it is not acted upon by a solution of potash either in the cold or with the assistance of heat. Concentrated sulphuric acid dissolves it, forming a conjugate acid, which furnishes a soluble crystalline salt with baryta. It is violently acted upon by fuming nitric acid. When the ebullition has been maintained for some time, a yellow substance separates, which, washed with water and redissolved in alcohol, is deposited, on the evaporation of this liquid, in needles resembling binitroanisole. On analysis it furnished—

Carbon.....	44·71	16 =	96	45·3
Hydrogen.....	4·03	8	8	3·8
Nitrogen	13·03	2	28	13·2
Oxygen.....	..	10	80	37·7

This compound differs therefore from phenetole only in having 2 equivs. of hydrogen replaced by 2 equivs. of hyponitric vapour; it is consequently the homologue of binitroanisole. I shall call it *binitrophenetole.*

When currents of sulphuretted hydrogen and ammonia are simultaneously passed through an alcoholic solution of this substance, sulphur is deposited; whilst the alcohol retains in solution a base which forms crystalline salts with sulphuric, nitric and hydrochloric acids, and which itself crystallizes in brown needles resembling nitroanisidine. It furnished on analysis—

Carbon.....	52·60	16 =	96	52·7
Hydrogen.....	5·41	10	10	5·5
Nitrogen	..	2	28	15·4
Oxygen.....	..	6	48	26·4

This compound, which may be represented by the formula $C^{16}H^{10}NO^2, NO^4$, would be derived from the substance $C^{16}H^{11}NO^2$ by the substitution of 1 equiv. hyponitric vapour for 1 of hydrogen. Designating the normal alkaloid by the name of phenetidine, we shall give to the preceding compound, which is homologous with nitroanisidine, the name of nitrophenetidine.

Binitrophenetole furnishes, when treated with an excess of nitric acid, a new crystalline product, which is probably trinitrophenitole. —*Comptes Rendus*, May 7, 1849.

ANALYTICAL CHEMISTRY.

On the Analysis of Organic Compounds which contain Chlorine. *By* Dr. Stædeler.

The analysis of organic substances by combustion with oxide of copper and the simultaneous employment of oxygen gas presents in many cases such decided advantages, especially in the examination of non-volatile substances containing a large amount of carbon, and is so easily executed, that it will not readily be exchanged for any other method. But if the compounds contain chlorine, very important differences may sometimes occur in the determination both of the carbon and the hydrogen; and these differences will be constantly noticed if the oxide of copper has served for several analyses. In this case the perchloride of copper formed is decomposed by the current of oxygen into oxide of copper and free chlorine, which increases the weight both of the chloride of calcium tube and of the potash apparatus.

That such a decomposition does occur may be detected by the taste of the air which is drawn through the chloride of calcium tube; it appeared however desirable to demonstrate it by a special experiment. For this purpose a quantity of oxide of copper was moistened with muriatic acid, and after being gently ignited, filled into a combustion tube, the ulterior extremity of which was connected with a thin glass tube, bent at right angles, through which the escaping gas was conducted into a cylinder filled with water containing a drop of mercury. When the oxide of copper was at a red heat, oxygen was passed over it; the gas which escaped quickly converted the mercury into calomel; the filtered liquid was rendered turbid both by sulphuretted hydrogen and by nitrate of silver, thus placing the evolution of chlorine beyond all doubt. In order to avoid the error which may arise from this circumstance in the analysis of organic substances containing chlorine, it is merely requisite to insert in the front of the combustion tube a spiral of thin sheet copper, and to keep this at a red heat during the combustion. The liberated chlorine then combines with the copper, and accurate results are obtained if no more oxygen is passed through the tube than is requisite for the perfect combustion of the substance, *i. e.* it should be discontinued as soon as a stratum of oxide begins to be formed upon the under surface of the copper spiral.—Liebig's *Annalen*, March 1849.

On the Separation of Antimony and Arsenic. *By* C. Ullgren.

When the antimony and arsenic are contained in a muriatic solution, the arsenic is converted by chlorine or an alkaline hypochlorite into arsenic acid, the solution mixed with a large excess of tartaric acid, then with a soluble salt of magnesia, and lastly supersaturated with ammonia. The basic arseniate of ammonia and magnesia falls, whilst not a trace of the antimony is precipitated. The precipitate

is washed with dilute ammonia. Both substances are now separated, and their amount can readily be determined according to the usual processes. However, in order to determine the amount of arsenic, without treating the magnesia-precipitate with muriatic acid and sulphuretted hydrogen, after previous reduction by sulphurous acid, the magnesian salt is dissolved in nitric acid, the solution evaporated to dryness in a platinum crucible, a weighed amount of calcined magnesia added to it, and the whole then formed with a little water into a thick paste, which is evaporated to dryness and heated to redness. In this manner the ammonia is expelled by the magnesia without any arsenic being reduced; which might easily happen if the solution in nitric acid were to be evaporated, and the residue heated alone to destroy the nitrate of ammonia. After deducting the amount of magnesia added, that of the arsenic acid is calculated from the residue, which contains $2MgO, AsO^5$. 100 parts of this salt correspond to 73·593 parts of arsenic acid or 48·018 parts of arsenic.—Liebig's *Annalen*, March 1849.

Observations on the Detection of Arsenic in Cases of Poisoning. *By* Prof. Wöhler.

To extract the arsenic and obtain it in the state of a liquid susceptible of filtration, the organic mass, as is well known, is changed or destroyed, according to its nature, by passing into it for a considerable time washed chlorine gas, disengaged by distilled sulphuric acid which has been tested; or by solution in concentrated caustic potash, saturation with muriatic acid and subsequent treatment with chlorine gas; or by solution in nitric acid which has been previously examined; or lastly, by solution in muriatic acid and the addition of chlorate of potash. The muriatic acid must likewise have been prepared with distilled sulphuric acid free from arsenic; as on the employment of crude oil of vitriol it almost always contains arsenic, as is frequently the case with that derived from chemical works. It is equally necessary to examine the chlorate of potash, for at present that which occurs in commerce frequently contains lead. The use of chlorine, either immediately or after previous solution of the mass in the smallest requisite quantity of caustic potash, undoubtedly deserves the preference in most cases.

After the excess of chlorine has been removed from the perfectly saturated mixture by long-continued digestion at a gentle heat, the liquid is filtered, saturated with a current of washed sulphuretted hydrogen, which should be passed into it for a day, then stoppered and set aside for at least twenty-four hours.

In order to reduce the arsenic to arsenious acid and facilitate its precipitation by sulphuretted hydrogen, the liquid may, it is true, be saturated or mixed with sulphurous acid, digested for a time, and the sulphurous acid then expelled by boiling. However, not much time is saved by this, as the sulphurous acid does not act instantaneously but very gradually. It is perhaps more advantageous to heat the liquid freed from chlorine to about 158° F., and to saturate

it at this temperature with sulphuretted hydrogen gas; as the arsenic acid is converted into sulphuret of arsenic, and precipitated quite as rapidly as the arsenious acid at the ordinary temperature.

The precipitate thus formed is allowed to subside, the excess of gas expelled by digestion at a gentle heat in an open vessel, the liquid decanted, the precipitate collected upon a small filter of Swedish paper, and carefully washed. The decanted and filtered liquid is again saturated with sulphuretted hydrogen, in order to make sure. This precipitate always contains, besides the sulphuret of arsenic, some organic sulphurous matter, which cannot be destroyed by nitric acid alone, but which it is absolutely necessary to destroy, because it might operate injuriously and give rise to error in the subsequent use of Marsh's apparatus, which in other respects is so sure and convenient.

This destruction of the organic matter is most readily and safely effected in the following manner:—The filter with the precipitate is placed in a sufficiently capacious crucible of real porcelain, concentrated nitric acid poured over it, and then digested until the whole is dissolved and forms a homogeneous mass. The free nitric acid contained in it is saturated by the gradual addition of pure carbonate of soda, and the mass cautiously evaporated to dryness. Everything now depends on the circumstance of its containing the requisite excess of nitrate of soda, which is readily effected by adding a sufficient quantity of nitric acid at first. The crucible is now heated over an Argand lamp gradually until the nitrate of soda fuses. At first the mass turns brown, then black, and melts quietly without any deflagration to a perfectly colourless transparent liquid. Every trace of organic matter is now perfectly destroyed, and the whole of the arsenic converted into arseniate of soda.

Concentrated pure sulphuric acid is now gradually dropped upon the cold hard saline mass in the crucible, and finally warmed with it until after the addition of excess of acid the whole of the nitric and nitrous acids have been *completely* expelled, and the mass is converted into bisulphate of soda. If nitric acid containing muriatic acid had been used for oxidizing the precipitate by sulphuretted hydrogen, volatile chloride of arsenic might be formed, and occasion a loss of arsenic. It is therefore requisite in this respect to ascertain the purity of the nitric acid and of the carbonate of soda.

The acid saline mass is now dissolved in the crucible in the smallest possible amount of hot water, and this solution then gradually poured, by means of a funneled tube in the usual way, into Marsh's apparatus, which has been previously exhausted of air and filled with hydrogen gas.

It should be observed, that, to hasten the production of arseniuretted hydrogen, the arseniferous liquid must contain no nitric acid; that this, therefore, must be completely expelled from the saline mass by the treatment with sulphuric acid.

To saturate the mass oxidized by means of nitric acid, carbonate of potash might be equally well employed; but soda was purposely directed, in case it were wished to seek for antimony in the poisonous

mass. This would then be contained in the fused mass in the state of antimoniate of soda. The mass should then be dissolved in water previous to treatment with sulphuric acid, and the insoluble antimoniate of soda collected upon a filter.

If the poisoned mass had contained copper, this would separate, on fusing the nitrate, as black oxide, and so betray its presence.

Whether the mirror formed in the glass tube by means of Marsh's apparatus consist of arsenic or of antimony is very readily determined, leaving out of question the difference of lustre, appearance, and other known characteristic differences, from the circumstance, that a mirror of antimony, when again heated in the current of hydrogen, is far more difficult to volatilize than arsenic; that it communicates not the least odour of garlic to the gas, and that it fuses previous to being volatilized. If it is examined with the lens after the spot has been heated over the spirit-lamp to redness, it is distinctly seen that the metal is fused at the margin, and has partly formed distinct bright globules of antimony—a peculiarity which is never seen with arsenic, because it does not fuse.

Nothing is now more easy than the detection of arsenic in an organic substance, even when this contains a mere imponderable trace; the great difficulty, and that which occasions anxiety and danger in such disagreeable tasks, is in the employment of reagents and apparatus to avoid the introduction of arsenic into the examination, and finding arsenic where in reality it did not originally exist.—Liebig's *Annalen*, March 1849.

Description of a new Process for detecting Iodine and Bromine. *By* M. Reynoso.

The method employed for detecting these substances when they exist in the state of iodides or bromides, consists in dissolving them in water, adding starch in the state of paste, or some æther and a few drops of chlorine water. The chlorine combines with the metal, setting free the iodine or bromine, which colours the starch blue or dissolves in the æther; but as iodine and bromine possess the property of combining directly with chlorine, forming a chloride of iodine or of bromine, the chlorine must not be employed in excess for detecting the presence of these bodies, because the chlorides of iodine or of bromine are decomposed in contact with water, producing hydrochloric acid and iodic or bromic acid, both of which are without action upon starch or æther.

This method requires great precautions, and is not at all applicable for the detection of minute quantities of iodides or bromides, especially when these substances are mixed with others capable of combining with the chlorine. It became therefore important to discover a substance which would isolate the iodine or bromine without acting upon them, however large an excess were employed. These conditions are all combined in oxygenated water; it decomposes hydriodic or hydrobromic acid, and has no action upon the liberated iodine or bromine.

The following is the mode of proceeding for detecting iodine :— In a small tube closed at one end is placed a fragment of deutoxide of barium, to which is then added some distilled water, pure hydrochloric acid and some starch paste; we then wait until some bubbles are seen to rise to the surface before adding the iodine; in an instant a pinkish-blue colour is evident if the quantity of iodine is very small, and a dark blue if it be considerable. It is advisable to make the experiment as directed, both as regards the manipulation, which is rendered very easy, and also as regards the success of the experiment. In this manner we are sure to employ an excess of oxygenated water, which is requisite when hyposulphites, sulphites or sulphurets are present; moreover, the hydrochloric acid employed in the preparation of the oxygenated water likewise plays an important part, for it serves to liberate the hydriodic acid—

$$BaO^2 + 2ClH + IH,\ KO + HO = BaO,\ ClH + KO,\ ClH + 2HO + I.$$

Although it is beyond doubt that hydrochloric acid, when acting upon the peroxide of barium in the presence of water, gives rise to the production of oxygenated water, I resolved to assure myself that it was the HO^2 which produced the result obtained. I therefore substituted tartaric acid for the hydrochloric acid, and obtained the same result.

The decomposition of hydriodic acid by pure oxygenated water had already been pointed out by M. Thenard.

When the iodides occur mixed with chlorides, sulphurets, sulphites or hyposulphites, the process is just as accurate; only, as by the action of the hydrochloric acid upon the sulphuret sulphuretted hydrogen is produced, which is decomposed by oxygenated water, and the sulphites and hyposulphites absorb oxygen in passing into the state of sulphates, a larger quantity of oxygenated water must be employed than if the iodide were pure.

The hyposulphites and sulphites, on their conversion into sulphates, produce a precipitate of sulphate of baryta in the liquid, which might arrest the reaction if the sulphate of baryta were not removed from the surface of the deutoxide of barium by agitation; this precaution moreover should never be neglected, in order to increase the production of oxygenated water. By this process I readily detected the presence of iodine in the urine of a patient to whom 0·10 centigramme of iodide of mercury was administered morning and evening, whilst chlorine failed to detect the presence of the iodine. This process likewise demonstrates the presence of iodides in the ash of the sponge. One drop of a solution of 0·010 grm. of iodide of potassium dissolved in a quart of water produces, each time that it falls into the tube, a blue colour sufficiently distinct at the surface. On agitating, the blue colour disappears, and the liquid acquires a rosy tint; on adding a fresh drop, the blue colour again makes its appearance at the surface. This method therefore readily indicates less than $\frac{1}{100000}$th of iodide of potassium.

The process is the same for bromine, except that, instead of starch, æther is added. It is agitated, when the bromine dissolves in the æther, and communicates to it a more or less dark yellow colour

according to the quantity present. But when we have a mixture of iodides and bromides, their presence may be ascertained by adding an excess of starch and æther; the iodine combines with the starch, whilst the bromine being taken up by the æther comes to the surface; and in this manner a blue colour is obtained below and a yellow colour above.—*Comptes Rendus*, April 30, 1849.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On some useful Properties of Benzole, and on a practical Mode of preparing it. *By* CHARLES BLACHFORD MANSFIELD, B.A.

BENZOLE dissolves many substances with extreme readiness and in large quantities, such as many resins, mastic, camphor, wax, fatty and essential oils, caoutchouc and gutta percha. Its volatility gives to its solution of either of the two latter substances the useful property of drying rapidly and perfectly; so that, when spread on glass or any polished surface, a film of the gum is deposited, which may readily be peeled off in the form of a tough membrane of any required degree of tenuity, and possessing all the properties of the original material. The same solutions, varnished on the skin, form admirable artificial cuticles, which have been found useful in cases of wounds and burns, and might probably be very beneficial in some skin diseases.

It dissolves gamboge in smaller quantity, and shell-lac even more sparingly; but it will mix in equal bulks with a saturated solution of lac in wood-spirit or alcohol. This property may be valuable to varnish-makers.

Copal and animè yield but slightly to the solvent power of this fluid; but its vapour, in the act of condensation, rapidly dissolves these resins; so that, if fragments of them be suspended in the head of a vessel in which the hydrocarbon is boiling, the vapour, as it condenses on their surfaces, softens and dissolves them, and trickles back into the vessel below, in which a colourless varnish will result, more or less concentrated according to the duration of the process.

Benzole dissolves quinine, depositing it on evaporation in a crystalline form; the condensing vapour dissolves the alkaloid, especially if not recently precipitated, more readily than the boiling liquid. Cinchonine it does not dissolve, but forms with it a bulky gelatinous mass. It dissolves strychnine and morphine but sparingly.

It dissolves iodine, phosphorus and sulphur; and when boiling takes up the latter in large quantity, of which however the greater part crystallizes out as the fluid cools.

It has been found extremely useful in the laboratory as a solvent in researches in organic chemistry, where the high price and almost

too great volatility of æther render a substitute for that agent a frequent desideratum.

It has an interest too as offering a cheap and ready source of many of the organic compounds of the benzoic series. Several beautiful bodies, which, from the comparative costliness of the parent materials, had only been obtained previously in very small quantities, may now be prepared in large bulk, such as nitrobenzole, nitraniline, &c. Dr. Hofmann has recently used coal-tar benzole, prepared by a method which will be described below, as a convenient source of aniline, of which base he has thus produced a large quantity for some researches in which he has been engaged.

The facility with which the vapour of benzole is taken up and retained by the air at its ordinary temperatures has been mentioned above. This property has been made to do service, with great success, in an apparatus for illumination, in which a stream of air, having passed through a reservoir of the volatile hydrocarbon, is conducted through pipes to the burners, at which, being ignited like coal-gas, it yields a light of extreme brilliancy and whiteness.

The property possessed by alcohol and pyroxylic spirit of burning with an almost lightless flame, so opposite to that of the highly carbonized benzole, renders it easy, by properly adjusting a mixture of the volatile oil with either of these spirits, to obtain a fluid which shall be readily vaporized, and shall yield a flame of any required degree of whiteness. Thus a mixture of 1 part by measure of benzole and 2 parts of spirit of spec. grav. about 0·840 forms an excellent fuel for a portable gas-lamp, which supplies itself with vapour by the heat which it generates in combustion. Any excess of spirit diminishes the luminosity of the flame, while too much of the other causes a tendency to smoke. Similar mixtures may be made of benzole with acetone, or with other inflammable liquids poor in carbon.

The inhalation of benzole vapours for the production of insensibility to pain is already on record as effectual.

The promises which benzole makes of utility are sufficiently numerous to encourage a belief that it may form a special object of manufacture and of commerce. It may be procured to any extent from coal tar or from the light naphtha in which it has hitherto been "wasting its sweetness on the desert air." If absolute purity be not required, it may be prepared, with very little expense and trouble, either in the laboratory or on the large scale in vast quantities; and by a further slight outlay of time, any required degree of purity may be ensured in the product. The description of a method which has been found to yield very satisfactory results may be not devoid of interest.

The boiling-point of benzole is the same as that of alcohol of spec. grav. 0·825 (176° F.); it is evident therefore that any of the summary processes of rectification which are practised by distillers in the manufacture of alcoholic spirits, are applicable to the separation of benzole from the less volatile fluids of the naphtha. The method now to be described is one which extracts nearly the whole

of this spirituous hydrocarbon by a very slight expenditure of time.

The light coal naphtha (of which it is best to take that which came over at the commencement of the distillation of the tar, and contains the benzole less diluted with substances having higher boiling-points) is placed in a metal retort, which is surmounted by an open vessel filled with water, and containing a worm or chamber, into which the vapour of the naphtha passes directly from the retort, and so arranged, that the less volatile fluids, which will be condensed in it, will flow back into the retort, or into a separate receiver, while the fluids more volatile than water will pass on in vapour to another condenser, which is kept as cold as possible. The water surrounding the still-head will gradually rise in temperature as the operation proceeds, and will at last boil; and when this takes place (or if the heating of the water be checked at any period of the process by addition of cold water), distillation will cease; for no fluid remains in the retort whose vapour is not condensable at the temperature of the head, which can never rise above 212° F. The distillate being rectified a second time in such an apparatus, keeping now the temperature of the head at or a little below 176° F., and reserving the part which comes over before the temperature in the retort has passed 194° F., a large proportion of a very volatile oil will be obtained, which, when exposed to a temperature of 4° F., will become solid to at least half its bulk. Of course, if the apparatus be double, the same result may be obtained by a single operation. A comparatively small quantity of a similar product may be obtained by receiving separately the first two or three gallons that run off from the common stills on the rectification of some hundred gallons of the light naphtha.

This produce should then be agitated with about a quarter of its bulk of oil of vitriol, or better still with about one-tenth of strong nitric acid, and then, after separation from this agent, with oil of vitriol as above. It should then be separated from the acid and distilled (or it may be distilled from the sulphuric acid), reserving again the portion given off below 194° F. The distillate, being tested by agitation with oil of vitriol, should remain perfectly colourless, and the acid should not now acquire a darker colour than a pale straw-brown; if it acquires a deeper tint, the process should be repeated. When this result is obtained, the oil should be well washed with water, and finally with an alkaline solution.

Its further purification may now be entrusted to its congealing property. It should be exposed to a temperature of about 4° F. (which may be conveniently attained by a mixture of ice and salt); the solid portion being then pressed and filtered, the result, after treatment with chloride of calcium, is fit for use.

The use of sulphuric acid in this process is to remove all the basic substances present, to oxidize the brown colouring matter (of which however but a small quantity accompanies the most volatile part of the light coal naphtha), and to remove such of the neutral oils as form compounds with oil of vitriol. Among these latter, an allia-

ceous oil, more volatile than benzole, is withdrawn, while the latter entirely resists the action of this acid even on being boiled with it. The nitric acid assists in the removal of the oxidable substances, and by forming a small quantity of fragrant nitrobenzole (which is left behind as residue on the distillation of the fluid), improves the odour of the product.—From the *Quarterly Journal of the Chem. Soc.*, vol. i. p. 261.

On a new Application of Platinum to painting upon Porcelain. By M. Salvetat.

When 1 part of platinum powder is mixed with 3 of a glass prepared with 3 parts minium, 1 part sand, and ½ part calcined borax, a gray of the very finest tone for porcelain is obtained, the advantages of which over all other gray colours are readily perceptible.

In all cases where the oxides of iron, cobalt, manganese and copper come in contact with a substance containing a large quantity of silica, and the temperature rises so high that the latter begins to fuse, the colour of the compound substance formed is always black, whether the oxide of cobalt was previously blue or not, the iron red or brown.

Upon this behaviour is based in general the process for preparing gray and black colours for painting upon porcelain or glass. Different tints and depths of colour are obtained by varying the proportions of the several oxides of iron, cobalt and zinc; and by adding the flux for the gray, the composition of which is given above, in greater quantity, a lighter and lighter gray is constantly obtained. But the blue colours consist of cobalt and zinc; and the freer the oxides are from iron, the more beautiful and pure is the blue. Peroxide of iron furnishes the red colours. Ochre-yellow is produced by oxides of iron and zinc; and these colours only exhibit a clean appearance when both these oxides are free from other metallic oxides, especially from the oxides of manganese and copper. It is evident therefore that the artist, when he wishes to modify the blue, red and ochre-yellow by mixing black or gray with them, has to form a mixture of peroxide of iron, oxide of cobalt and oxide of zinc in undetermined proportions, the colour of which is black; so that he is only able from very great practice to determine in advance the tint and intensity of the colour. Moreover, as the tone of the colour after the burning is not the same as before, since the blue and red tints may be altered, nay have even entirely disappeared, he is unable to give the painting the appearance it will have after the firing. This is a serious inconvenience, especially in the painting of figures.

The platinum gray is free from all these evils. As it contains no cobalt, it may very well be mixed with red and ochre-yellow; nor does it affect the blue, as it contains no oxide of iron. It produces in a mixture only that tint which is peculiar to it, and retains it even after the burning. Platinum gray can moreover always be prepared of the same tint. The platinum powder is readily obtained

by calcining ammonio-chloride of platinum, and it has then only to be mixed in the above proportions with the flux. Platinum is not the only metal which can be used for gray colours for porcelain; all those metals which constitute the platinum ores can, when properly diffused, be employed with greater advantage than the gray from the oxides of iron and cobalt. The author has tried palladium and ruthenium; the former gives a paler gray than platinum, and ruthenium, a gray with a brownish-red tint. The sesquioxide of iridium has long been employed by M. Frick for black colours for porcelain, and experience has shown that it is preferable to all other similar colours. The author has since 1845 furnished more than 100 grms. of iridium gray for the Sèvres manufactory, where it is in daily use. Platinum gray may be advantageously substituted for it; it is cheaper, its tone more agreeable and its preparation more easy. It is likewise more generally distributed; and during the year that this colour has been used, experience has proved its value; it is now generally employed at Sèvres.—*Ann. de Chim. et de Phys.*, xxv. p. 342.

Method of soldering Cast Iron with Wrought Iron.

The following process has been recommended for this purpose:—First melt filings of soft cast iron with calcined borax in a crucible; then pulverize the black vitreous substance which is thereby produced, and sprinkle it over the parts which are intended to be united; after which heat the pieces of cast and wrought iron and weld them together on an anvil, using only gentle blows. This method is peculiarly applicable for the manufacture of iron articles which are intended to be made red-hot, and are required to be impervious to fluids or liquids, as such a result cannot be obtained by simple fastening.—*Technologiste*; and Newton's *Journal*, May 1849.

Test for ascertaining the Value of Uranium Ores. By A. Patera.

This new process for ascertaining the amount of uranium in uranium ores is said to furnish a quick and accurate result. The ores generally consist of pitchblende, mixed with iron and copper pyrites, sulphuret of lead, &c. A weighed quantity is dissolved in pure nitric acid, the liquid filtered from the insoluble silica, and mixed with an excess of carbonate of potash. We thus obtain neutral uranate of potash in solution, contaminated with arsenic and sulphuric acids if these are present. All the other metals are precipitated as carbonates, and are removed by filtration. The neutral uranate of potash is evaporated in a gilt silver dish to dryness, and heated to redness, when biuranate of potash is formed, which is insoluble in water, is very easily washed, and from which the amount of uranium can readily be calculated. A similar process might perhaps be used in the preparation of uranium on a large scale.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Action of Nitric Acid upon Sebacic Acid.
By ADOLPH SCHLIEPER.

IT is generally asserted that sebacic acid is not altered by treatment with nitric acid; but the similarity of many of its physical properties with benzoic acid authorized the conjecture, that, like the latter, it might be converted into nitrosebacic acid, $C^{10}H^7O^3NO^4$. In all cases it was interesting to know, if the action of nitric acid on this constant product of decomposition of oleic acid at high temperatures did not cause the formation of one or more of those acids which Laurent produced by direct action of this agent upon oleic acid.

The sebacic acid employed in this research was obtained by dry distillation of the crude commercial oleic acid. The distillate was boiled with water several times, the watery extracts saturated with carbonate of soda and evaporated to dryness, to remove the caprylate and caprinate of soda; the dry saline mass was then exhausted with hot absolute alcohol, which left the sebacate of soda undissolved. The latter was then dissolved in water, and the sebacic acid precipitated by addition of muriatic acid; after being purified by repeated crystallizations from water, it presented itself as a loose, very light, white mass, consisting of small shining scales.

To ascertain whether any formation of nitrosebacic acid takes place, 1 part of sebacic acid was heated with 20 to 30 parts crude nitric acid, spec. grav. 1·4, in a spacious matrass; no solution is effected in the cold, but it takes place perfectly a little below the boiling-point; at the same time the orange-coloured vapours of hyponitrous acid and the like colour which the liquid assumes indicate a decomposition of the sebacic acid. The nitric solution was then kept at a continual slow boiling on a sand-bath, in such a manner that the evaporating nitric acid condensed for the greater part in the long neck of the matrass, and flowed back. After two to three hours boiling, a small part of the solution was poured out, to see if the formation of nitrosebacic acid had taken place, though the continual but very slow development of red vapours indicated clearly that the decomposition was not yet finished.

The hot nitric solution, mixed with 8 to 10 times its volume of

cold water, separated a great quantity of probably unaltered sebacic acid, which having been washed and dried, showed all the physical properties of that substance. I prepared and analysed the silver salt of the acid so obtained, and thus proved that it was only unaltered sebacic acid. 0·312 grm. of the silver salt gave 0·161 grm. silver, which corresponds to an amount of oxide of silver of 55·41 per cent. Sebacate of silver contains 55·76 per cent. oxide of silver.

I may here mention an easy method of obtaining perfectly snow-white sebacic acid, this material having generally a yellowish tint. It is sufficient just to boil 1 part of impure sebacic acid with 5 to 6 parts of nitric acid, spec. grav. 1·35, and then mix the solution with a great quantity of boiling water; on cooling, the sebacic acid crystallizes perfectly pure.

The rest of the solution of sebacic acid in nitric acid was kept continually boiling till the entire cessation of the formation of nitric oxide, constantly renewing the evaporating nitric acid. The oxidation takes place very slowly; it required eight days for about 200 grs. of sebacic acid. After the solution had changed its orange to a nearly white colour, and the development of nitric oxide had ceased, the contents of the matrass were poured into a flat basin, diluted with an equal volume of water, and the nitric acid slowly driven off on the water-bath, using the precaution of adding from time to time a small quantity of water. The white residue was then dissolved in water, filtered and evaporated to a syrup on the water-bath, then allowed to crystallize over sulphuric acid. Regular crystals could not be obtained, perhaps because the quantity of the solution was not sufficient; but the whole solution solidified very soon, and became a white crystalline mass somewhat adhesive, appearing like pure grape-sugar crystallized in a similar way. This substance, in a perfectly pure state, is a strong acid, and the only product which results from the action of nitric acid on sebacic acid. It is, as will presently be proved, identical in composition and properties with pyrotartaric acid, as far as a comparison was possible with the knowledge we possess of the latter.

For analysis, the acid was dried over sulphuric acid, and afterwards melted, but without sustaining any loss in its previous weight. It was burnt with chromate of lead, and gave the following results:—

Carbon	45·27	45·42	5 =	30	45·45
Hydrogen	6·09	6·09	4	4	6·06
Oxygen	48·64	48·49	4	32	48·49

Hence 1 equiv. of sebacic acid assimilates 5 equivs. of oxygen on treatment with nitric acid, and is resolved into 2 equivs. of the hydrate of pyrotartaric acid:—

1 equiv. of sebacic acid ..... $= C^{10}H^8O^3$
5 equivs. of oxygen ..... $= O^5$

2 eq. of the hydrate of pyrotartaric acid $= C^{10}H^8O^8 = 2(C^5H^3O^3,HO)$.

This acid thus differs from lipic acid, which it resembles in many properties, only by 1 equiv. less of oxygen. The acid in question has the following qualities, which coincide very nearly with those of pyrotartaric acid, as stated by Pelouze. The very slight deviations in regard to the crystallization of the acids it was impossible for me to reconcile, on account of the small quantity of the new acid at my command. The acid forms a perfectly white slightly crystalline mass, a little adhesive, and permanent in the air; heated in the water-bath, it became semifluid; but heated a few degrees above 212° F., it melted into a clear fluid, solidifying when cooled into a crystalline mass. Heated very cautiously on platinum, it volatilizes entirely, evolving a white suffocating vapour. Heated between two watch glasses, it sublimes, leaving a carbonaceous residue, in very shining prismatic needles, which show all the reactions of the unsublimed acid. The acid is inodorous, and has a very acid taste, similar to that peculiar to succinic acid. It is easily soluble in water, alcohol and æther, also in concentrated sulphuric acid, without being decomposed. Heated with alcohol and sulphuric acid, the æther of this acid is readily formed, which is distinguished by a peculiar aromatic odour. The watery solution expels carbonic acid with effervescence, and forms gummy salts with potash, soda and ammonia when evaporated briskly, but whose concentrated solutions, allowed to evaporate over sulphuric acid, dry to crystalline masses. The ammonia salt loses ammonia on evaporation, and becomes acid. The alkaline salts are soluble in alcohol; furnish no precipitates with baryta and lime salts; with chloride of iron a flocculent brownish-red precipitate, soluble in a pretty large quantity of boiling water; and with copper salts a light green precipitate. With acetate of lead no precipitate results; but after two to three hours, the mixture of the solutions, not too much diluted, deposits a white lead salt in granules, principally adhering to the sides of the vessels; once separated, they are difficultly soluble in water. If an addition of alcohol is made to the mixed solutions of acetate of lead and the ammonia salt of the acid, a thick white precipitate is produced directly, melting to small drops when heated, and evidently the same precipitate which deposits after a longer standing of the solutions, without the addition of alcohol. The ammonia salt gives with basic acetate of lead a thick curdy precipitate, cohering after some hours, easily soluble both in acids and in an excess of basic acetate of lead. Nitrate of silver is precipitated by the ammonia salt in white flakes, very like freshly precipitated alumina.

All these properties agree so perfectly with those of pyrotartaric acid as described by Pelouze, that, considering the similarity of the composition of both acids, I do not hesitate in the least to proclaim the identity of pyrotartaric acid with the acid obtained by the oxidation of sebacic acid with nitric acid.

From the statements of Weniselos my own differ only in regard to the ammonia salt, which that chemist states he obtained in fine crystals; and in regard to the neutral lead salt, which ought to deposit itself after a certain time in fine needles, whereas Pelouze,

as well as myself, obtained only granulated precipitates under the same conditions.

For further analysis I selected the silver salt, which was prepared by precipitating the nitrate of silver with the ammonia salt of the acid; but I am sorry to say that I did not succeed in obtaining it of a constant composition, which is very remarkable in a silver salt. I procured from salts of two different preparations 2 to 3 per cent. of oxide of silver less than the formula AgO, PT required; though the acid combined with it, calculated by itself, after deduction of the mean amount of oxide of silver, corresponded exactly to the formula of the anhydrous acid.

The silver salt is very sensible to light; dries slowly, and forms semitransparent hard pieces, very like the dried hydrate of alumina, which become brownish-white when powdered. The analysis gave the following results:—

	First preparation.		Second preparation.	Calculated according to $C^5H^3O^3$, AgO.
Silver....	64·11	64·01	64·88	67·05
Carbon ..	18·88	..	18·34	17·35
Hydrogen	2·06	..	1·97	1·73
Oxygen..	..	..	..	13·87

The lead precipitate which is produced by basic acetate of lead in the ammonia salt furnished on analysis 73·21, 72·70 and 73·0 per cent. oxide of lead, which amount corresponds exactly with the formula $2(PbO, C^5H^3O^3)+PbO, HO$. The identity of this acid with pyrotartaric acid can hardly be doubted; however, a further comparison will only be possible when the latter has been submitted to a more accurate examination.—Silliman's *Journal*, May 1849.

On Devitrification. By D. C. Splitgerber.

The author shows, in accordance with Fournet's statements, that there is a crystalline and an amorphous devitrification, both of which are produced by the decomposition of the constituents of the glass into different new opake compounds, of which we have analogous examples in obsidian and the slags.

Devitrification is produced under various circumstances; for instance, when the glass is very frequently heated and cooled in the furnace, especially when it contains much lime and alumina; it loses its conchoidal fracture and its transparency;' its vitreous lustre is converted into a waxy lustre; and finally the mass becomes quite porcellaneous. This change proceeds from the surface to the interior.

A slight loss of alkali, which is volatile at a high temperature, cannot be avoided in this operation; but this is not the cause of the opacity, as the loss of alkali is never very considerable, and as transparent glass can be made with a still less amount of alkali, and moreover the devitrified mass can be remelted into good glass without any further addition. The cause must rather be sought for

in a resolution of the original composition of the glass into other opake compounds in the softened mass.

A very remarkable case of devitrification was obtained by allowing a crucible containing soda glass to cool very slowly; a devitrified crust, 6 to 7 millimetres in thickness, had formed on the surface of the good glass, whilst a crucible with potash glass close to it had remained quite unaltered. This crust, which is accurately separated from the transparent glass, and appears at first sight quite amorphous, contains in the uppermost opake portion, on careful examination, a tissue of minute crystals, which are difficult to detect in the nearly opake mass, whilst the lower portion presents not a trace of crystallization; we have here then a crystalline and an amorphous devitrification together, in which most probably the small crystals were last formed in the opake mass.

Notwithstanding the great physical difference of the glass and the crust externally, their specific gravity is very close; the specific gravity of the crust was 2·503, whilst that of the subjacent glass was 2·485. This difference was found to be quite constant in several weighings. We have here something similar to what happens in Vesuvian and garnet, which in the crystalline state exhibit a greater density than after fusion, which renders them amorphous and vitreous.

No differences worth mentioning were found in the analyses of the two masses; they are both sexsilicates:—

The glass.			The crust.		
75·73 SiO^3	containing	39·35 O	76·27 SiO^3	containing	39·63 O
13·18 NaO	...	3·40 O	13·06 NaO	...	3·37 O
9·58 CaO	...	2·73 O	9·32 CaO	...	2·66 O
1·51 Al^2O^3	...	0·70 O	1·35 Al^2O^3	...	0·63 O

On another occasion, when the cooling had been effected more rapidly, some opake white granules had formed in the vitreous mass, around which regular phænomena of polarization were exhibited, showing the tension caused in the glass. It may be assumed that the above-described crust had originated from an agglomeration of similar granules, which in the slow cooling had time to form.

On another occasion some similar granules had formed at the bottom of the melting furnace in impure potash glass, or rather in some glass slag. This distinctly showed a tendency to a regular formation of crystals, but which had been prevented by the tenacity of the mass, they being frequently six-sided prisms, but without sharp edges and surfaces. On analysis it exhibited considerable resemblance to the crystallized glass analysed by Dumas. It furnished—

Silica	69·34	containing	36·00 oxygen.
Potash.....	13·94	...	2·36 ...
Lime	11·31	...	3·21 ...
Alumina	5·41	...	2·52 ...

In the plombiferous glass slag in the collection of Prof. H. Rose, and which was presented to him by Prof. Faraday, the author ob-

served some perfectly similar six-sided crystals, but which were much sharper and more developed, probably from the mass being more readily fusible than the above.

Devitrification was moreover met with in various glass mixtures containing lime when the firing had been continued for several hours; acicular crystals separated, but which again dissolved and disappeared at a higher temperature. The potash glass bore a much larger addition of lime than the soda glass.

The author then describes some experiments on the volatilization of the alkali. They show that its quantity is dependent on various concomitant causes, and increases when the temperature is continued for a long time, and especially with a greater addition of lime. It was also found that soda is far more readily volatilized in the furnace than potash.—*Berlin Berichte*, Feb. 1849.

On the Composition of Bone Earth. By Dr. W. Heintz.

It has hitherto been generally admitted, according to an analysis by Berzelius, that the phosphate of lime contained in bones has the composition $8CaO, 3PO^5$; a few chemists have expressed a different opinion; however, it is in general a mere supposition, or not supported by satisfactory experiments. To decide the question, the author made the following analyses. The bones, broken into small pieces, were first deprived of all soluble salts by means of water, and then reduced to a fine powder. A portion of this powder was employed for the determination of the carbonic acid; another portion was carbonized, the cinder exhausted with muriatic acid, then burnt, and the small imponderable quantity of ash added to the acid solution. The liquid, strongly concentrated by evaporation, was supersaturated with a large excess of carbonate of soda, evaporated to dryness, and the residue fused, in order to convert any pyrophosphoric acid that might have been formed into the ordinary modification of this acid. The fused mass was then dissolved in muriatic acid, and the lime, phosphoric acid and magnesia were determined according to known methods. Three analyses were made in this way; the fourth was slightly modified, inasmuch as the bone powder was exhausted with muriatic acid without having been previously carbonized, so as to avoid the objection that, in the carbonization of the bones, a small quantity of the phosphoric acid may have been decomposed and have been lost. The following are the results of these analyses:—

	Bone of ox.	Bone of sheep.	Human bone.	
Lime	37·46	40·00	37·89	37·51
Magnesia	0·97	0·74	0·57	0·56
Phosphoric acid	27·89	29·64	28·27	28·00
Carbonic acid	3·10	3·08	2·80	2·81
Water, fluorine and organic matter	30·58	26·54	30·47	31·12

Or if we assume the carbonic acid to be combined with the lime,

and the phosphoric acid with the magnesia and lime, and indeed with the greatest possible amount of these bases, we have—

	Bone of ox.	Bone of sheep.	Human bone.	
Carbonate of lime.....	7·07	7·00	6·36	6·39
Phosphate of magnesia..	2·09	1·59	1·23	1·21
Phosphate of lime	58·30	62·70	60·13	59·67
Lime.....	1·96	2·17	1·81	1·62
Water, fluorine and organic substance	30·58	26·54	30·47	31·11

It is evident, therefore, from these analyses, that the amount of the bases in the bones exhausted with water is greater than the acids contained in them are capable of combining with. The question then arises, whether other acids do not exist in it besides the carbonic and phosphoric acids. The author could not detect muriatic or sulphuric acid in the cold prepared nitric extract of bones which had been previously exhausted with water and then carbonized; but he succeeded in detecting the presence of fluorine in it, confirming in this respect the statements of Berzelius, Frerichs and Erdmann; and he was therefore inclined to assume that the excess of lime may have been combined with the fluorine, which, on evaporating the muriatic solution, must have escaped for the greater part in the state of hydrofluoric acid. According to the analyses of Berzelius, a human femur contains 3·0 per cent. and the bone of an ox 4·5 per cent. of fluoride of calcium in 100 parts of the fixed constituents. Marchand found 1 per cent. fluoride of calcium in human bone corresponding to 1·6 per cent. of the bone ash.

The author endeavoured to determine the amount of fluoride of calcium contained in the human bones used for the above analyses. He found 2·05 per cent. fluoride of calcium, corresponding to 2·97 per cent of the bone ash. If the amount of fluoride of calcium be calculated from the quantity of lime contained in the human bones beyond that required to saturate completely the phosphoric and carbonic acids, we find 3·57 and 3·24 per cent. of their ash. This agrees so closely with the amount directly found, that we are led to the conclusion that the inorganic constituents of bones must contain, along with neutral carbonate of lime and fluoride of calcium, phosphate of lime and magnesia, having the composition represented by the formula $3RO, PO^5$; and that Berzelius's statement, according to which the lime salt has the composition $8CaO, 3PO^5$, is incorrect. If, for instance, this last composition were correct, the excess of lime would be so great that the bones would appear to contain more than 7 per cent. of fluoride of calcium. The quantity of the fluoride of calcium in bone ash would even exceed 10 per cent. So great an amount of this salt has never been detected in it, and can therefore not be admitted. We are consequently justified in admitting that the phosphate of lime is contained in bones of the form $3CaO, PO^5$.

The author has likewise found that bones which have been exhausted with water contain not a trace of iron. In those cases

therefore in which it has been detected it must have arisen from colouring matter of the blood, which can be completely removed from the bones by cold water, and is therefore not an essential constituent of the fixed principles of bones.—*Berlin Berichte*, Feb. 1849.

On some Compounds belonging to the Quinone Series. *By* Prof. F. Wöhler.

It had hitherto remained doubtful whether the atomic weight of quinone should be represented by $C^{24} H^8 O^8$ or $C^{12} H^4 O^4$. The author now shows that the latter is most probably the correct one, as it agrees with the found composition of all the compounds belonging to the quinone series. This is the case with the sulphur compounds prepared and previously described by the author*, the composition of which has been corrected according to the following formulæ, founded upon new analyses. In connexion with these corrections, the author describes some new and highly remarkable sulphur compounds of hydroquinone.

Brown Sulphohydroquinone, $C^{12} H^5 O^4 S^2$.—This substance, as is well known, is produced by passing sulphuretted hydrogen into a solution of quinone, with the precaution that a little of the latter is left unaltered. It has now been ascertained that its formation is accompanied and caused by the simultaneous production of green hydroquinone, which, on account of its sparing solubility, is precipitated at the same time, and is mixed in variable quantity with the sulphur compound, the colour of which it causes to vary between blackish-brown and reddish-brown. This admixture, which had formerly escaped observation, is the reason why the former analysis gave the amount of carbon too high and that of the sulphur too low. 2 equivs. quinone and 2 equivs. sulphuretted hydrogen produce 1 equiv. sulphohydroquinone, $C^{12} H^5 O^4 S^2$, and 1 equiv. green hydroquinone, $C^{12} H^5 O^4$.

Yellow Sulphohydroquinone, $C^{12} H^6 O^4 S$, is produced when the preceding substance is suspended in water and submitted to the further action of sulphuretted hydrogen. It is best obtained by saturating a solution of quinone in alcohol with sulphuretted hydrogen, when sulphur separates in minute crystals. It is moreover produced likewise with the separation of sulphur, by saturating an alcoholic solution of the brown sulphohydroquinone with sulphuretted hydrogen. This separation and admixture of free sulphur was formerly overlooked, which explains the incorrect results of the former analyses. The pure compound is yellowish, crystalline, and fuses even below 212° with partial decomposition. Its alcoholic solution gives with acetate of lead a white precipitate, proving apparently that it does not contain the sulphur in the form of sulphuretted hydrogen. By pouring a solution of quinone over it, it is converted into brown sulphohydroquinone, with simultaneous production of green and colourless

* Chem. Gaz., vol. ii. p. 487.

hydroquinone, the formation of which in this reaction had also been overlooked.

2 equivs. yellow sulphohydroquinone furnish with 1 equiv. quinone, 1 equiv. brown sulphohydroquinone, and at the same time 1 equiv. colourless and 1 equiv. green hydroquinone.

In the formation of this yellow sulphur compound, the elements of 1 equiv. sulphuretted hydrogen combine with the 1 equiv. of the brown compound in such a manner that the 2 atoms of sulphur contained in the latter are eliminated from the combination.

The substances formerly described under the name of *chlorosulphoquinone* are probably merely mixtures of products containing chlorine and sulphur.

Hydrosulphate of Hydroquinone.—Colourless hydroquinone, $C^{12} H^6 O^4$, has the remarkable property of combining in two proportions with sulphuretted hydrogen, forming two beautifully crystalline bodies, which evidently contain the sulphuretted hydrogen as such.

a. The Rhombohedral Hydrosulphate, $3(C^{12} H^6 O^4)+2HS$, is formed when sulphuretted hydrogen is passed into a cold saturated solution of colourless hydroquinone. It forms very regular transparent rhombohedrons, is void of smell and unalterable in dry air. When moistened with water, it instantly disengages the odour of sulphuretted hydrogen; and when its solution is heated to boiling, it is readily decomposed into sulphuretted hydrogen and colourless hydroquinone. It behaves in the same manner with alcohol, and also on fusion alone. With acetate of lead it is converted into pseudo-crystals of black sulphuret of lead. On analysis it furnished—

	I.	II.		Calculated.
Carbon	58·70	..	36	59·37
Hydrogen	5·51	..	20	5·48
Sulphur	8·86	8·71	2	8·81
Oxygen	26·93	..	12	26·34

The amount of sulphur in II. was determined from the quantity of sulphuret of lead formed with acetate of lead; the amount of sulphur in I. was ascertained in the usual manner by heating the crystals with a mixture of calcined marble and nitre, and precipitating the sulphuric acid with a salt of baryta.

b. The Prismatic Hydrosulphate, $2(C^{12} H^6 O^4)+HS$, is formed when sulphuretted hydrogen is passed into a saturated hot solution (at about 104°) of colourless hydroquinone; it forms very long colourless prisms, totally different in form from the preceding, but perfectly similar in their behaviour. They furnished on analysis 6·76, 6·95 and 6·66 per cent. sulphur. The above formula requires 6·77.

It is highly probable that the compound $C^{12} H^6 O^4+HS$ likewise exists; this would contain 12·6 per cent. sulphur.

Combination of Hydroquinone with Acetate of Lead, $2PbO,\overline{A}+C^{12} H^6 O^4+3HO$.—Perhaps it would be more correct to regard it as $(PbO,\overline{A}+C^{12} H^6 O^4)+(PbO,\overline{A}+3HO)$. It was accidentally

obtained in the analysis of the hydrosulphate of hydroquinone with a solution of acetate of lead. It is immediately produced when colourless hydroquinone is dissolved in a moderately concentrated hot solution of acetate of lead. It forms oblique rhombic prisms, is very sparingly soluble in cold, but readily soluble in hot water without decomposition. It parts with its water of crystallization at 212°. The crystals become milk-white, retaining their form even up to 356°; they then fuse, and are decomposed. No corresponding combination with hydroquinone appears to exist.—Liebig's *Annalen*, March 1849.

On the Chlorinated Products of Decomposition of Quinic Acid. *By* Dr. G. Stædeler.

When quinic acid is distilled with a mixture for evolving chlorine, a violent disengagement of carbonic acid results; whilst an acid liquid, and a yellow crystalline sublimate which condenses in the tube through which the vapours are conducted, are obtained.

The liquid contains formic acid, and the same oily substance in solution which is produced under similar circumstances from starch, and which was formerly described by the author by the temporary name *a*-oil. It is a very general product of the decomposition of organic substances by chlorine; and the author hopes soon to be able to give further details respecting its composition and properties.

The crystalline sublimate is a mixture of four substances, which, as regards their composition, are members of the quinone series. They may be viewed as quinones, in which 1, 2, 3, or the whole of the equivalents of hydrogen have separated, and are replaced by a corresponding number of equivalents of chlorine. All the members of this group possess the peculiarity of quinone of combining with hydrogen, and forming with it combinations analogous to the hydroquinones. The last member is already known; it is the chloranile discovered by Erdmann; to the others the author has assigned the names of *chloroquinone*, *bichloroquinone* and *trichloroquinone*.

To separate these substances, the mixture is first exhausted with cold alcohol, which dissolves chloroquinone and trichloroquinone, whilst bichloroquinone and chloranile, which are only soluble in boiling alcohol, are left behind. Chloroquinone and trichloroquinone are precipitated from the alcoholic solution by water, then dissolved in a small quantity of boiling alcohol, and separated from each other by crystallization. To separate the bichloroquinone from the chloranile, the two are dissolved in boiling alcohol, when bichloroquinone separates on cooling in brilliant lemon-coloured crystals, and the chloranile in very delicate iridescent laminæ, which can easily be poured off the heavy crystals of bichloroquinone.

I. *Chloroquinone*, $C^{12} H^3 Cl O^4$.—It has hitherto been found impossible to separate the chloroquinone perfectly from trichloroquinone; a mixture of laminæ and needles was always obtained, which consisted, according to the analyses, of nearly equivalent proportions of the two substances ($= C^{12} H^3 Cl O^4 + C^{14} H Cl^3 O^4$). It might

also be concluded from the analyses, that it was a combination of equivalents of chloroquinone and trichloroquinone with a slight excess of the latter; but so far as the eye was able to decide, the quantity of laminæ was far greater than would correspond to such an inconsiderable impurity; and moreover the compound, freed as much as possible from trichloroquinone, agrees so closely in its properties with quinone, that we are compelled to adopt the view that it is a quinone in which 1 equiv. hydrogen is replaced by 1 equiv. chlorine. It crystallizes in very delicate, sometimes in long yellow needles, which fuse even at 212° to a dark yellow oily liquid; and which communicate to the skin, and to organic substances in general, a purple colour, like the salts of gold. It has a peculiar aromatic odour and an acrid burning taste; it is readily soluble in æther, alcohol and concentrated acetic acid; less so in boiling water, and almost entirely insoluble in cold water. With cold concentrated sulphuric acid it forms a reddish-yellow solution, which in a few minutes solidifies to a paste of very delicate white prisms. When sulphurous acid is poured over it, it assimilates hydrogen, and is converted into brown or colourless chlorohydroquinone according to the amount of acid; it however could not be obtained pure any more than the chloroquinone, and consequently was not analysed.

II. *Bichloroquinone*, $C^{12} H^2 Cl^2 O^4$, separates from the boiling saturated alcoholic solution in minute, shining, bright lemon-coloured crystals, and from a mixture of alcohol and æther in dark yellow prisms several lines in length. They have a faint aromatic odour and scarcely any taste. They melt at 302° to a reddish liquid, which on solidification reacquires its former colour. Bichloroquinone is insoluble in water and cold alcohol, but readily soluble in æther, boiling alcohol and boiling acetic acid. Dilute solution of caustic potash dissolves it with a reddish-brown colour, with the production of a new acid, which closely resembles chloranilic acid. It is not decomposed by concentrated sulphuric, nitric or muriatic acids; sulphurous acid converts it into bichlorohydroquinone.

Colourless Bichlorohydroquinone, $C^{12} H^4 Cl^2 O^4$, is obtained when bichloroquinone is boiled with a sufficient quantity of sulphurous acid; as the colourless solution cools, it separates in long flat needles or in short thick prisms, which are but sparingly soluble in cold, but readily in boiling water, as also in alcohol, æther and hot acetic acid. It likewise dissolves without decomposition in hot concentrated sulphuric and muriatic acids. Nitric acid converts it into bichloroquinone, whilst perchloride of iron or nitrate of silver change it into

Violet Bichlorohydroquinone.—The same substance is produced when an aqueous solution of colourless bichlorohydroquinone is boiled with bichloroquinone. It separates from the dark brown solution in small, dark, violet, or long, flat, blackish-green needles, of equal beauty with the green hydroquinone. It is almost insoluble in cold, but soluble in boiling water and in hot acetic acid, on the cooling of which it again separates unaltered. Its composition cor-

responds to the formula $C^{12} H^3 Cl^3 O^4 + 2HO$; it consequently contains just as much hydrogen as the very similar green hydroquinone. It is unaltered in the air; but dried over sulphuric acid or heated to about 158°, it loses its 2 atoms of water, and passes into *yellow bichlorohydroquinone*. The same compound is formed on adding alcohol, æther or concentrated sulphuric acid to the violet bichlorohydroquinone. Concentrated nitric acid converts it into bichloroquinone.

The Yellow Bichlorohydroquinone, $C^{12} H^3 Cl^2 O^4$, melts at about 248° to a red liquid, and is decomposed into bichloroquinone and white bichlorohydroquinone, which are deposited in the cold portion of the tube in isolated crystals. It has a burning aromatic taste, and a faint odour resembling bichloroquinone. It dissolves in alcohol, æther, boiling water, hot acetic acid, and also in concentrated sulphuric acid, without decomposition. On the cooling of the aqueous, or on slow evaporation of the ætherial solution, there is always a partial conversion of the yellow into the violet compound.

III. *Trichloroquinone*, $C^{12} HCl^3 O^4$, forms large golden laminæ, which melt at 320°, and sublime even at 266° pretty rapidly in delicate laminæ resembling chloranile. It has no smell, and does not colour the skin when perfectly free from chloroquinone. It is insoluble in cold water, sparingly soluble in cold alcohol and acetic acid, but readily soluble in æther, boiling alcohol and boiling acetic acid, even when they are diluted with an equal volume of water. It dissolves in concentrated sulphuric and nitric acids without decomposition; by the action of potash, a salt of a new acid separates in long red needles, which dissolve in water with a wine-red colour; and on mixing the solution with muriatic acid, the acid falls in red crystals. Concentrated ammonia appears to produce a compound analogous to chloranilammon.

When trichloroquinone is boiled with a sufficient quantity of sulphurous acid, it dissolves; and on evaporating the colourless solution,

Colourless Trichlorohydroquinone, $C^{12} H^3 Cl^3 O^4$, separates in heavy oily drops, which solidify into crystalline masses on cooling. Once separated, the trichlorohydroquinone is very sparingly soluble in cold water; it melts in boiling water, and gradually dissolves. It is readily soluble in æther and in alcohol; and the solutions, which have an acid reaction, furnish a white precipitate with neutral acetate of lead. Concentrated sulphuric acid dissolves it without decomposition; concentrated nitric acid converts it into yellow trichloroquinone. On mixing the solution with nitrate of silver or perchloride of iron, a compound separates in minute yellow laminæ, which appear under the microscope to be very oblique four-sided prisms, and which seem to be a combination of trichloroquinone with 1 equiv. hydrogen, or

Yellow Trichlorohydroquinone.—This compound was discovered some time ago by Woskressensky, by passing chlorine over quinone, then subliming the chlorinated product in a current of the gas, and purifying it by recrystallization from alcohol. He however erro-

neously supposed that this substance was formed by the quinone exchanging 3 equivs. hydrogen for an equal number of chlorine, and called it chloroquinoyle. According to Woskressensky's view, therefore, chloroquinoyle, for which subsequently the name chloroquinone was substituted, would have the same composition as trichloroquinone; which however is not confirmed by his analyses nor by the properties of this substance, which are totally different from those of trichloroquinone. Woskressensky's chloroquinoyle, from its properties as well as from its composition, is a hydrogen compound of trichloroquinone, and its formula is $C^{12} H^2 Cl^3 O^4$.

IV. *Chloranile*, $C^{12} Cl^4 O^4$.—It has already been stated in what manner chloranile can be separated from the other solid products which are formed in the distillation of quinic acid with a mixture for generating chlorine. It is however always obtained only in small quantity. Erdmann first procured it by the action of chlorine upon an alcoholic solution of chlorisatine and bichlorisatine; and subsequently other processes for its preparation were described by Fritzsche and Hofmann. Its properties, and principally the products of its metamorphoses by alkalies, have been minutely investigated by Erdmann. There remains its behaviour towards sulphurous acid, which distinctly proves chloranile to be a member of the quinone series.

Colourless Chlorohydroanile.—When chloranile is boiled with a solution of sulphurous acid and water, the yellow colour of the crystals is gradually changed into a dirty white; they are collected on a filter, washed with water, dried, and dissolved in a mixture of æther and weak spirit, when the colourless chlorohydroanile separates on the slow evaporation of the æther in groups of delicate nacreous laminæ. They are usually coloured somewhat brownish by some foreign substance, which is insoluble in boiling concentrated acetic acid, and can so be separated from the chlorohydroanile.

Its composition is expressed by the formula $C^{12} H^2 Cl^4 O^4$. Under exactly the same circumstances as quinone and chloroquinone, chloranile has likewise combined with 2 equivs. hydrogen; and we may consequently regard chloranile as a quinone in which the whole of the hydrogen has been replaced by chlorine.

Chlorohydroanile experiences no change at 302°, at 320° it is slightly browned, and between 415° and 420° it becomes dark brown and begins to sublime very rapidly; when heated more strongly, it melts. It is obtained in long, flat, colourless needles by sublimation in a current of air; it has neither odour nor taste; is perfectly insoluble in water, but readily soluble in alcohol and æther; the solutions redden blue litmus-paper, and are precipitated by neutral acetate of lead. They are neither dissolved nor altered by concentrated sulphuric acid even on the application of heat; dilute solution of caustic potash dissolves it readily without any colour, and it is again separated by acids in a crystalline state. The hot saturated solution in potash deposits on cooling prismatic slightly coloured crystals, which however quickly turn red in the air. The solution in ammonia is yellow, and becomes, when exposed to the air, quickly

green, and finally red, with separation of a chrome-green crystalline precipitate.

When treated with water which contains some perchloride of iron or nitric acid, the colourless chlorohydroanile is not altered in the cold, but at a gentle heat it turns yellow. Nitrate of silver acts in the same manner when an alcoholic solution of it is used; metallic silver is deposited as a mirror or in the form of a gray powder, and from the filtered boiling solution delicate yellow rhombic prisms separate on cooling, which appear to be a compound of chloranile with 1 equiv. hydrogen.

Hypochlorite of soda converts chlorohydroanile into a substance crystallizing in minute green prisms, which however was not further examined.—Liebig's *Annalen*, March 1849.

ANALYTICAL CHEMISTRY.

On the Estimation of Arsenic. *By* Henry Rose.

The best method of separating arsenic acid from its solutions, when its quantity has to be determined, is decidedly that which Levol proposed, that of precipitating it in the form of arseniate of ammonia and magnesia. Levol recommends calcining the dried precipitate, in order to convert it into $2MgO, AsO^5$, from which compound the amount of arsenic acid can be calculated. But this furnishes an erroneous result, for the arsenic acid is reduced at a high temperature by the ammonia, and a loss results, which becomes greater the longer the ignition is continued. The weight of the precipitate should be determined either by drying it over sulphuric acid, or, better still, *in vacuo*, or by exposing it to a temperature of 212° F. until it no longer decreases in weight. In the first case, the precipitate has the composition $2MgO + NH^4O + AsO^5 + 12HO$; in the latter case, $2MgO + NH^4O + AsO^5 + HO$.

When the arsenic is contained in solution in the state of arsenious acid, it must first be converted into arsenic acid, in order to determine it as arseniate of ammonia and magnesia. This is best effected by means of chlorate of potash and hydrochloric acid, taking care to avoid a strong or long-continued heat, as otherwise some arsenic might be volatilized in the form of chloride.

Even when arsenic is precipitated from a solution by sulphuretted hydrogen, its amount is best ascertained by converting the sulphuret, without previously determining its weight, by means of chlorate of potash and hydrochloric acid, into arsenic acid, and then precipitating this as arseniate of ammonia and magnesia. When arsenic is contained in a solution in the state of arsenious acid, its amount can be very accurately ascertained by means of a solution of chloride of gold. From the amount of gold reduced, the quantity of the arsenious acid can be calculated.

In most of the salts of arsenic acid which are insoluble in water, the bases can be separated from the acid by fusion with carbonated alkali. This even succeeds with those arseniates the corresponding phosphates to which cannot be perfectly decomposed in this manner, for instance with arseniate of lime. However, this mode of decomposition is not easily executed, on account of the nature of the vessels which we are compelled to employ; for platinum crucibles are too much acted upon by the operation, and in using porcelain crucibles silica is dissolved.

The method employed to separate phosphoric acid from strong bases, that by means of metallic mercury and nitric acid*, may also be employed to effect the separation of arsenic acid from the same bases. But it is not possible to determine the amount of arsenic in the separated arseniate of the protoxide of mercury, as it cannot be fused with carbonated alkali without violently acting upon the vessels.

The separation of arsenic from tin is best effected by converting the metals into sulphurets, and heating them in an atmosphere of sulphuretted hydrogen, when the sulphuret of arsenic is volatilized, and its vapours can be passed into solution of ammonia whilst the sulphuret of tin is left behind. Long after experiments on this subject had been made, the author found that Ebelmen had recently proposed a similar method for their separation†.

The separation of arsenic from antimony can be effected according to two methods. The first method is essentially similar to that which the author proposed some time back to separate tin from antimony. The oxidized compound is fused with hydrate of soda, and the mass, after disintegration in water, treated with dilute alcohol, with which the antimoniate of soda is also washed, it being insoluble in it. The second method can be used, especially when the two metals are contained as acids in a solution. Tartaric acid and chloride of ammonium are added to the solution, and the arsenic acid then precipitated as arseniate of ammonia and magnesia; the antimonic acid remains in solution, from which it can be precipitated, after being acidified by hydrochloric acid, as sulphuret of antimony. This method can also be employed to distinguish a mirror of antimony from one of arsenic, when they have been obtained by Marsh's method.

With respect to the separation of arsenious from arsenic acid, Levol has proposed to separate the arsenic acid as arseniate of ammonia and magnesia. The amount of the arsenious acid however can be very readily ascertained by means of perchloride of gold.—*Berlin Berichte*, 1849.

On the Estimation of the Sugar of Milk, and Determination of the Richness of Milk. *By* Prof. Poggiale.

As none of the processes hitherto known furnish a quick and accurate indication of the richness of milk, I imagined that if we could

* Page 202 of the present volume. † *Ib.*, p. 82.

determine without the balance, by the method of volumes, one of its constituent elements, the problem would be solved. I believe I have succeeded in attaining this result by ascertaining the proportion of the sugar of milk. Several samples of pure milk have been submitted to chemical analysis.

The following is the mean of ten analyses:—

Water	862·8
Butter	43·8
Sugar of milk	52·7
Caseine	38·0
Salts	2·7
	1000·0

Thus, according to my experiments, 1000 grms. of milk contain 52·7 grms. of sugar. M. Boussingault found, in a series of observations, a mean of 50 grms., a difference which is undoubtedly owing to the processes followed for its determination. The quantity of sugar contained in milk is considerable, and moreover presents but slight variations. The process which I propose is the application of that of M. Barreswil* to the estimation of the sugar of milk, which, like glucose, reduces the salts of copper; and the proportion of salt of copper decomposed will afford the amount of sugar of milk.

Preparation of the Test-Liquor.—This is prepared by adding to a solution of sulphate of copper bitartrate of potash, and dissolving the precipitate which is formed in caustic potash. The strength of the alkaline solution is then determined with great care, from the quantity of sugar employed to decolorize a known volume of the liquid. It is important to observe that milk-sugar, and not cane-sugar, must be employed in this operation. I made several experiments in order to avoid the determination of the strength of the solution of binoxide of copper, which is decidedly the longest and most delicate experiment. The following proportions constantly furnished a liquid, 20 cubic centimetres of which correspond to 0·200, or 2 decigrammes of whey:—

Crystallized sulphate of copper	10 grammes.
Crystallized bitartrate of potash	10 ...
Caustic potash	30 ...
Distilled water	200 ...

The filtered liquid is perfectly clear and of an intense blue colour.

Preparation of the Whey.—To determine the amount of sugar of milk, it is indispensable to separate the fatty matter and the caseine by coagulation. This is easily effected by placing 50 or 60 grms. of the milk in a small flask, adding to it a few drops of acetic acid, and then raising the temperature to between 104° and 122°. A transparent liquid is obtained on filtration. According to my experiments, 1000 grms. of milk yield 923 grms. of whey, which gives for 1000 grms. of whey about 57 grms. of sugar.

Examination of the Whey.—20 cubic centimetres of the test-

* Chem. Gaz., vol. ii. p. 544.

liquor are introduced by means of a pipette into a small flask, which should be preferred to a porcelain capsule, as it allows of the liquid being seen from top to bottom, and of observing with the greatest ease the moment the decolorization is complete. The liquid is then boiled. On the other hand, a burette, each division of which is equal to a fifth of a cubic centimetre, is filled with the whey, and this poured drop by drop into the liquid, agitating the latter continually, and heating it after each addition of whey. This is continued until the blue tint has entirely disappeared. At first a yellow precipitate of hydrated protoxide of copper is formed, which however soon turns red and sinks to the bottom of the flask. When the operation is terminated, the quantity of whey employed is read off the burette, and the weight of sugar contained in 1000 grms. of whey determined by rule of three.

I admitted above that 1000 grms. of whey contain 57 grms. of sugar; we must however not be particular about a few grammes more or less. The most usual adulteration, the addition of water, is easily detected by estimating the sugar. It is however possible that the cream might be removed without any addition of water, or with the addition of cane-sugar or sugar of milk. In this case I determine by a simple and quick process the quantity of fatty matter, by adding acetic acid to the milk, boiling, and agitating it after cooling with æther, which removes the butter. The ætherial solution is decanted and evaporated. It is frequently advisable to repeat the examination of the whey, which, as all the arrangements are made and the strength is nearly known, does not occupy more than one or two minutes.—*Comptes Rendus*, April 16, 1849.

On the Analysis of Organic Compounds which contain Chlorine. By Dr. Augustus Vœlcker*.

In a notice in No. 159 of the 'Chemical Gazette,' it is reported that Dr. Stædeler of Göttingen observed important differences in the determination both of the carbon and the hydrogen, when organic substances containing chlorine were burned with oxide of copper and the simultaneous employment of oxygen gas. He ascribes these differences to the action of the current of oxygen gas, which decomposes the chloride of copper produced into oxide of copper and free chlorine, which increases the weight both of the chloride of calcium tube and the potash bulbs. That such a decomposition really takes place, Dr. Stædeler has shown by actual experiment; and he has likewise devised a process by which good results may be obtained in the analysis of organic substances containing chlorine. This process consists in placing in the front of the combustion-tube a spiral of thin sheet copper, which is kept red-hot during the combustion. The copper, according to Stædeler, retains the liberated chlorine, provided the current of oxygen is stopped as soon as a stratum of oxide begins to be formed upon the surface of the copper spiral.

I have been in the habit of burning organic substances with oxy-

* Communicated by the Author.

gen gas, kept in a gas-holder, from which it is passed through several chloride of calcium tubes and tubes containing caustic potash, in order to secure its purity and complete dryness before it is allowed to enter the combustion-tube; but I have latterly preferred to generate a current of oxygen gas in the combustion-tube itself, by placing a mixture of chlorate of potash and oxide of copper at the closed end of the tube, because I experienced great difficulties in securing the absolute dryness of the oxygen by the above arrangement.

If the first method is made use of, as is generally done in the Göttingen laboratory, no difficulty in stopping the current of oxygen gas at the right point will be experienced; but if the second is preferred, it will be found, I think, not at all easy to discontinue the evolution of oxygen just at the right moment. Though I have no doubt that good results may be obtained if this is done, and if the front of the combustion-tube is not kept too hot, yet I think that it requires considerable experience to prevent the sublimation of subchloride of copper; and it appears to me almost impossible to obtain the hydrogen correct if the organic substance contains much chlorine.

It is indeed well known that subchloride of copper is volatile; and it has therefore been recommended to burn organic substances containing chlorine with chromate of lead instead of oxide of copper, because in this case the chlorine of the subchloride of copper combines with lead, and is retained in the tube as chloride of lead. But if oxide of copper alone is employed, subchloride of copper is volatilized and condensed in the chloride of calcium tube; and hence the hydrogen will be obtained too high.

The combustion with oxide of copper, in addition to a current of oxygen gas, presents, as Dr. Stædeler justly observes, such decided advantages and is so easily executed, that it will not readily be exchanged for any other method; and, I may add, it will be preferred to the combustion with chromate of lead in all cases where the latter can be dispensed with. Now, where chlorine is present, I am certain the combustion can be executed in the usual way, and good results will be obtained if the oxide of copper is mixed with one-fifth to one-eighth of pure litharge. Any chloride or subchloride of copper which may be formed during the combustion of organic substances containing chlorine will be decomposed, and the chlorine be detained in the tube as chloride of lead.

Professor Mulder of Utrecht is in the habit of mixing the oxide of copper for organic analyses with one-fifth to one-eighth of pure litharge, because he found that by this addition the oxide of copper is rendered so much less hygroscopic that the use of the air-pump can be dispensed with with the greatest safety, provided the tube is rapidly filled with the mixture still warm. Having frequently had the opportunity of experiencing in Professor Mulder's laboratory the decided advantage of his suggestion, I have great pleasure in recommending it to all chemists occupied with the study of organic chemistry, particularly because it is available in ordinary combustions as well as in the analysis of organic substances containing chlorine.

The tube is filled as usual, first placing a mixture of about 60 to 70 grs. of fused and powdered chlorate of potash and an equal quantity of oxide of copper at the closed end of the combustion-tube; then 3 inches of the mixture of oxide of copper and lead; after which the organic substance mixed with the oxides, and so on as usual. I may however observe, that the basic chloride of lead formed during such combustions is not altogether non-volatile; for which reason it is advisable to keep the front of the combustion-tube not too hot, and to regulate the current of oxygen gas so that it does not pass through the tube too rapidly. If the oxygen gas is disengaged too quickly and the front of the combustion-tube is kept at a high red heat, I have observed sometimes a slight white sublimate in that part of the combustion-tube which is placed outside of the furnace; but even in these unfavourable circumstances I have not seen it proceed further or enter the chloride of calcium tube. It appears therefore that the basic chloride of lead is a great deal less volatile than the ordinary chloride, which indeed is more readily volatilized than some perhaps may imagine.

In order to be certain that no material error is committed by following this method of analysing organic substances containing chlorine, and to prove that no such decomposition takes place with chloride of lead as that which Dr. Stædeler observed by passing oxygen over red-hot chloride of copper, I thought it advisable to make the following experiment. A quantity of oxide of copper was dissolved in muriatic acid, the solution evaporated to dryness, and the resulting salt very gently heated. The salt was found to redissolve perfectly in water. It was then mixed with oxide of copper and oxide of lead; and with this mixture a combustion-tube of ordinary size was filled, at the closed end of which the usual quantity of chlorate of potash and oxide of copper was situated. The proportion of chlorine in the chloride of copper used in this experiment was at least three times as large as the amount of chlorine which can be contained in the quantity of an organic substance which is to be analysed. The open end of the combustion-tube was then shut with a cork, through which a glass tube bent at right angles was passed. The longer vertical arm of this tube dipped into a cylindrical glass filled with distilled water, and containing a drop of mercury. After having ascertained that the cork and tube fitted air-tight in the combustion-tube, the latter was raised gradually to a red heat, and oxygen passed over it for about twenty minutes. During this time the gas which escaped by the glass tube through the water did not produce any change, and left the surface of the mercury perfectly shining. The water was not precipitated by nitrate of silver, nor was any change of colour produced by the addition of hydrosulphuret of ammonia; showing that no chlorine or chloride had reached the water.

It may be inferred therefore that the above method can be safely recommended for the analysis of organic substances containing chlorine.

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PROCEEDINGS OF SOCIETIES.

Royal Society.

Feb. 1, 1849. (George Rennie, Esq., Treasurer, Vice-President, in the Chair). The following paper was read :—

"On the Chemistry of the Urine;" in three Parts. By H. Bence Jones, M.D., M.A., F.R.S.

Part I. *On the variations of the Acidity of the Urine in Health.*

The mode of examination adopted by the author was the following: Two test solutions were made; the one with carbonate of soda; the other with dilute sulphuric acid, of such strength that each measure of a graduated tube, when filled with either solution, was equivalent to one-twelfth of a grain of dry and pure carbonate of soda.

A weighed quantity of urine was neutralized by one or other of the test solutions, and thus the degree of acidity or alkalescence was determined.

Diurnal variations in the acidity of the urine were observed. The acidity of the urine was found to ebb and flow; it was greatest a short time before food was taken, and was least about three hours after breakfast, and five or six hours after dinner, when it reached the minimum point; after which it again increased, and attained the maximum point previous to food being again taken.

If no food was taken, the acidity varied but slightly for twelve hours.

By comparing the effect of vegetable food with animal food, it appeared that the food which irritated the stomach most and caused most secretion of acid in the stomach, caused the greatest oscillations in the urine.

Dilute sulphuric acid taken in large doses produced but little effect on the variations of the acidity of the urine; but it was proved to increase the acidity of the urine.

Part II. *On the simultaneous variations of the amount of Uric Acid and the Acidity of the Urine in a healthy state.*

The result of these experiments is, that there is no relation between the acidity of the urine and the amount of uric acid in it. The urine that was most acid contained least uric acid; that which contained most uric acid was not most acid. All food causes an increase in the amount of uric acid in the urine; and there is no decided difference between vegetable and animal food, either as to the increase or diminution of the amount of uric acid in the urine.

Part III. *Variations of the Sulphates in the Urine in the healthy state, and on the influence of Sulphuric Acid, Sulphur and the Sulphates, on the Sulphates in the Urine.*

The result of these experiments is, that the sulphates in the urine are much increased by food, whether it be vegetable or animal. Exercise does not produce a marked increase in the sulphates. Sulphuric acid, when taken in large quantity, increases the sulphates in the urine. In small quantity, even when long-continued, no effect on the amount of sulphates is manifest.

Sulphur taken as a medicine increases the sulphates in the urine. Sulphate of soda and sulphate of magnesia produce the most marked increase in the sulphates in the urine.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

Observations on Styracine. *By* F. Toel.

Liquid storax obtained from the bark of *Styrax officinalis* contains, as is well known, a neutral crystalline substance, styracine, the peculiar nature of which has hitherto remained unexplained. From the author's researches it follows that the composition of the substance is expressed by the formula $C^{60}H^{28}O^{6}$, and that it is a combination of cinnamic acid having a perfectly analogous constitution to the natural fats.

By the action of a hot concentrated solution of the hydrate of potash it is resolved into cinnamic acid and a new substance, for which the name *styrone* is proposed. The liquid product previously obtained by this mode of decomposition, and described under the name of *styracone*, was a mixture resulting from the employment of impure styracine.

Styrone, $C^{42}H^{23}O^{5}$, distils over with the water, whilst a solution of cinnamate of potash is left in the retort. No other product is formed in this operation. The distillate is turbid, but in a short time becomes transparent and filled with a bulky tissue of small acicular crystals of styrone. It forms thin silky needles, has a very agreeable odour resembling hyacinths, melts at 91°, is volatilized without decomposition at a higher temperature, and again solidifies on cooling into a crystalline mass. It is tolerably soluble in water, and most readily so in alcohol, æther and styrole. It is well characterized by its peculiar mode of crystallization from water. When a hot saturated solution is set aside to cool, it becomes milky, and only begins to clear after some hours, becoming filled with minute acicular crystals. When observed under the microscope while still turbid, this milkiness is seen to result from innumerable drops of oil, which gradually, and frequently quite suddenly, seem to disappear and to dissolve; and in their place, all at once, a crystal makes its appearance, which grows perceptibly by attracting and absorbing the surrounding drops of oil. It is scarcely to be doubted that this phænomenon consists in a transition from the liquid amorphous into the crystalline state. The oily styrone might however also be a loose combination with water, and the phænomenon consist in a separation of this water.

When styrone is treated with manganese and sulphuric acid, it affords oil of bitter almonds, like styracine.

If the composition of styrone found in three accordant analyses is examined more closely, and compared with that of styracine, which has likewise been ascertained with certainty by the author, together with the circumstance that the latter is converted by the action of alkali into cinnamic acid and styrone, no other probable mode of explaining the process offers itself than that styracine is a conjugate combination of cinnamic acid with a substance represented by the formula $C^{42}H^{21}O^3$, which on its separation from the acid assimilates the elements of 2 atoms of water, and is thus converted into styrone. This substance, which cannot be isolated, might be called *oxide of styryle* $=C^{42}H^{21}O^3$, in conformity with the name of oxide of lipyle, which is converted into glycerine on separation from the fatty acids. According to this view, styracine would be a combination of 1 equiv. oxide of styryle with 1 equiv. cinnamic acid.

Chlorostyracine, $C^{60}H^{21}Cl^7O^6$, is produced by the action of dry chlorine upon styracine. It forms a yellow, tenacious, viscid mass of an acrid taste and faint odour; it is insoluble in water, soluble in alcohol and æther, and not crystallizable.

Chlorocinnamic Acid, $HO+C^{18}H^6ClO^3$, is produced by the action of an alcoholic solution of potash upon chlorostyracine, with the simultaneous production of a chlorinated oily substance and of chloride of potassium. It forms long, shining, flexible needles, has no smell, melts at 270°, sublimes, is slightly soluble in cold water, and very readily soluble in alcohol and æther. The salts it forms with the alkalies, the alkaline earths and oxide of silver are crystalline. It is not identical with the chlorocinnamic acid described by Stenhouse.

It follows from its composition and mode of production, that chlorostyracine may be regarded as a conjugate combination of 1 equiv. chlorocinnamic acid with 1 equiv. of an oxide of chlorostyryle, $C^{42}H^{15}Cl^6O^3$, which, on its separation from the former, is converted into the above-mentioned chlorinated oil, which however cannot contain all these 6 equivs. of chlorine, since chloride of potassium is simultaneously formed. This chlorinated oil is heavier than water and colourless; but becomes brown so quickly in the air that it could not be analysed with any degree of confidence.—*Göttingen Berichte*, p. 54, 1849.

On the Action of Phosphoric Acid upon Cholesterine. *By* C. Zwenger.

Cholesterine is readily decomposed by concentrated phosphoric acid with the assistance of heat; the products resemble those obtained by means of sulphuric acid*, and are likewise solid, well-characterized hydrocarbons, which however differ decidedly in their physical properties from those previously described.

* Chem. Gaz., vol. vi. p. 373.

If 1 part of cholesterine is boiled with from 6 to 8 parts of concentrated phosphoric acid until the temperature of the liquid has risen to 278°—the melting-point of cholesterine—the cholesterine melts, but at the same time experiences complete decomposition. Care must be taken not to increase the temperature beyond this point or to let the mixture fuse too long, as otherwise secondary products of decomposition are formed. Previous to melting, the cholesterine loses its crystalline appearance, and becomes slightly yellowish.

The decomposed cholesterine furnishes with water a dirty white soft mass; the decanted phosphoric acid contains but mere traces of organic matter in solution. The decomposed mass consists of two new hydrocarbons, one of which I shall call *a*-cholesterone, the other *b*-cholesterone.

a-Cholesterone.—To prepare this substance, the decomposed cholesterine, after being freed as much as possible from phosphoric acid by washing with hot water, is exhausted with boiling alcohol. The first portion usually contains some free phosphoric acid, and the *a*-cholesterone crystallizes with difficulty from it, and is best set aside. By repeated exhaustion with boiling alcohol, the whole of the *a*-cholesterone may be removed; and the solution deposits it on cooling in long slender needles. On boiling the decomposed cholesterine with alcohol, the entire mass melts, and is converted into a yellow oily liquid, which on cooling again solidifies; but the more *a*-cholesterone is removed from it, the less fusible does the residue become, until finally, when the whole of the *a*-cholesterone has been dissolved, a slightly yellowish, somewhat resinous solid substance is left in small quantity, which consists principally of *b*-cholesterone.

The crystals of *a*-cholesterone are purified by frequent crystallization from absolute alcohol; they are right-rhombic colourless prisms of considerable lustre, and which, on slow crystallization, frequently attain to the length of half an inch. They melt at 154° to a clear colourless liquid, which usually becomes solid only when perfectly cold and after long standing. At a higher temperature *a*-cholesterone boils, and may be distilled almost unaltered; the yellowish distillate solidifies after some time to a radiately-crystalline mass; when ignited, it burns with a smoky flame. It is easily decomposed by chlorine, with evolution of muriatic acid. It experiences a similar oxidation by nitric acid as the hydrocarbons separated by sulphuric acid. Sulphuric acid colours it red. It is insoluble in water; very sparingly soluble in cold, but readily soluble in boiling alcohol, and the more so the more concentrated the alcohol. The greater portion separates on cooling; it is very soluble in æther, in essential and fatty oils; is void of taste and odour, and is lighter than water. It furnished, on combustion with chromate of lead—

				Mean.
Carbon	87·60	87·73	87·77	87·70
Hydrogen.....	12·06	12·17	12·12	12·12

b-Cholesterone.—The residue insoluble in alcohol is exhausted with boiling æther, in which it dissolves the more readily the more

resinous constituents are contained in it; otherwise the solution is effected with difficulty. The ætherial solution deposits, on cooling and evaporation, *b*-cholesterone in the form of a white crystalline mass of a faint lustre, which, by exhaustion with alcohol and repeated recrystallization from æther, can be readily freed from adherent *a*-cholesterone, as also from a resinous substance.

b-cholesterone dissolves in æther with difficulty even with the assistance of heat, very sparingly in alcohol, and not at all in water. On the other hand, it is readily dissolved by the essential and fatty oils. It crystallizes from the ætherial solution in extremely slender and somewhat silky white needles. *b*-cholesterone melts at about 347°, and solidifies on cooling to a transparent, crystalline, brittle mass. It cannot be distilled at a higher temperature without partial decomposition; it burns with a smoky flame. It behaves in general like the other hydrocarbons towards chlorine, nitric and sulphuric acids. It is likewise void of taste and smell, and lighter than water. On combustion with chromate of lead it furnished—

			Mean.
Carbon	87·56	87·88	87·70
Hydrogen	12·14	11·98	12·04

Consequently both the *a*- and *b*-cholesterone possess precisely the same per-centage composition as the hydrocarbons separated by sulphuric acid. *b*-cholesterone has, it is true, upon the whole, some resemblance to *b*-cholesteriline; it is however readily distinguished by its melting-point being about 144° lower, and by its never crystallizing in laminæ like the *b*-cholesteriline, but always in very slender needles.

By the action of phosphoric acid, cholesterine is resolved almost entirely into *a*- and *b*-cholesterone, if the temperature is not raised above the melting-point of cholesterine. In all cases a greater amount of *a*-cholesterone is obtained. Generally there is also a small quantity of a resinous substance, contained partly in the alcoholic, but principally in the ætherial solution from which the *b*-cholesterone crystallized. The quantity of this substance is considerably increased when the decomposition has not been conducted with care; and it then occasions loss of substance, and renders the purification of the hydrocarbons more or less difficult. This resinous substance, which I have sometimes obtained perfectly colourless and transparent, is probably nothing but an amorphous hydrocarbon similar to *a*-cholesteriline. Its properties and composition I have not examined more minutely.

In the analysis of these hydrocarbons, a loss of carbon may readily occur if the combustion has not been executed with the greatest care. This experience, and the circumstance that the amount of hydrogen of all the hydrocarbons separated from the cholesterine is almost equal to that of the cholesterine, induced me to submit this substance to fresh analysis. Perfectly pure fused cholesterine furnished on combustion with chromate of lead—

Carbon.....	84·24
Hydrogen	12·04
Oxygen	3·72

These numbers however agree perfectly with the previous analyses of other chemists.

Cholesterine therefore is readily decomposed by sulphuric and phosphoric acids. These acids deprive it of water; they do not require to be in a very concentrated state; phosphoric acid, which boils at 278°, contains nearly 60 per cent. of water; and the mixture of sulphuric acid and water, which decomposes cholesterine at 158°, contains about 45 per cent. of water. It is this easy separation of the water which principally supports my view that cholesterine is the hydrate of a hydrocarbon. The most remarkable circumstance in this decomposition is the vast amount of solid hydrocarbon that can be obtained from cholesterine; I am not acquainted with any substance which exhibits the slightest resemblance to it in this respect. It has been concluded, on hypothetical grounds, that many hydrocarbons, for instance naphthaline, must be combinations of several hydrocarbons; and it is highly probable that cholesterine contains the hydrate of a hydrocarbon of very complex nature, the readily decomposable material of which instantly experiences on its elimination a further decomposition or separation by the action of acids.

In my first paper on cholesterine, I stated that the almost identical per-centage composition of the various hydrocarbons did not justify us in admitting them to be isomeric or polymeric; I then advanced the formula $C^{81}H^{66}+3HO$ for cholesterine; and showed that, by the splitting up of this formula, hydrocarbons might be obtained, which, without being isomeric or polymeric, might yet nevertheless possess nearly the same per-centage composition. The determination of the atomic weight of the several hydrocarbons can alone decide this question. This however is accompanied by very considerable difficulties, and I have not yet succeeded in obtaining satisfactory results.

If we consider the occurrence of cholesterine in the living organism, its sparing solubility in the fluids of the body, and at the same time its appearance in inexplicable masses, we are directed by its chemical constitution to suspect the original hydrocarbon, or perhaps its proximate constituents, to pre-exist in the blood; cholesterine would then be formed simply by the assimilation of water, and would immediately separate on account of its insolubility. It cannot be denied that this hypothesis, when all the appertaining phænomena are considered, possesses some probability, which is increased by the fact, that I am led to believe that a substance standing in a direct relation with cholesterine actually exists in the blood, but upon which subject I shall communicate more details upon a future occasion.—Liebig's *Annalen*, March 1849.

On Xanthoproteic Acid. By M. Van der Pant.

Xanthoproteic Acid from Albumen.—Coagulated albumen is reduced to a fine powder, and exposed for 168 hours to the action of a mixture of 2 parts water and 1 of commercial nitric acid. A great

portion remains undissolved. Water is added, the sediment washed with water, the fat removed by æther, dried in the air, again reduced to a fine powder, and then dried at 266° F.

The acid dissolves entirely in ammonia, forming a dark brown liquid. If the ammoniacal solution of the acid is evaporated to dryness in the water-bath, it no longer redissolves so readily in water. To prepare the salts of copper, lead and baryta, the xanthoproteate of ammonia is evaporated to the consistence of a syrup, and then diluted with water. Xanthoproteic acid, prepared as above and dried at 266°, furnished on analysis—

	I.	II.	III.	IV.	V.	
Carbon	50·48	50·45	50·16	49·91	50·25	50·50
Hydrogen	6·61	6·51	6·35	6·21	6·42	6·30
Nitrogen.....	15·28	14·77	14·90	14·57	14·84	15·15
Oxygen	26·47	27·11	27·43	28·15	25·29	
Sulphur	1·09	1·09	1·09	1·09	1·09	27·15
Ash.....	0·07	0·07	0·07	0·07	0·07	

I. to IV. were made with the acid as originally obtained, V. with acid which had been dissolved in ammonia. The composition is the same, the ammonia being expelled at 266°. The colour however continues of a much darker colour, but this is produced by a mere trace of ammonia. The barytic compound yielded 13·11 per cent. baryta, and for the organic substance—

	I.		II.	
Carbon.....	45·15	51·96	45·17	51·97
Hydrogen.....	5·40	6·22	5·34	6·18
Nitrogen	12·63	14·53	12·63	14·53
Oxygen	..	27·29	..	27·33
Sulphur				

The copper salt, obtained by precipitating xanthoproteate of ammonia with acetate of copper, is a green precipitate, which after washing and drying furnishes a dark green salt. Dried at 266°, it gave on analysis 12·9 per cent. oxide of copper, and for the organic substance—

	I.		II.	
Carbon	44·89	51·53	46·90	52·76
Hydrogen.....	5·80	6·65	5·73	6·40
Nitrogen	13·89	15·97	12·63	14·20
Oxygen	..	25·85	..	26·64
Sulphur				

Xanthoproteic Acid from Hair.—Horse-hair was treated for fourteen hours with a mixture of 1 part nitric acid and 2 parts water, washed with water and dried. A considerable amount of gas was disengaged upon adding the acid, and the mass then changed into a dark brown liquid, upon which floated a thick layer. The acid was of a dark brown colour, and furnished when dried at 266°—

Carbon	48·91	49·24	49·50	49·23
Hydrogen	5·80	5·70	6·34	6·30
Nitrogen	14·13	15·03	14·74	14·90
Oxygen	29·11	27·98	27·37	27·52
Sulphur	1·92	1·92	1·92	1·92
Ash	0·13	0·13	0·13	0·13

Xanthoproteic Acid from Proteine.—Coagulated albumen was dissolved in very dilute solution of caustic potash and sulphurous acid passed into the solution until there was no further reaction of sulphur upon acetate of lead. A small precipitate which was formed was separated by filtration; the solution precipitated with acetic acid; the precipitate, after having been freed from adherent acetic acid by washing and from fat by æther, was treated for fourteen hours with a mixture of 1 part nitric acid and 3 parts water, mixed with water, poured upon a filter, washed and dried at 266°. It furnished—

			Mean.
Carbon	50·97	50·74	50·86
Hydrogen	6·56	6·65	6·60
Nitrogen	14·76	14·90	14·83
Oxygen	26·23	27·23	26·23
Sulphur	1·48	1·48	1·48

The baryta salt of this xanthoproteic acid prepared from proteine, when dried at 212°, furnished 12·69 per cent. baryta, and for the organic substance—

	I.		II.	
Carbon	45·75	51·40	45·62	52·25
Hydrogen	5·09	5·84	5·27	6·03
Nitrogen	12·69	14·50	12·63	14·46
Sulphur Oxygen	..	27·36	..	27·26

Xanthoproteic Acid from Cow's Horn.—The horn was freed from the outermost layer, and exposed for 48 hours to the action of 1 part nitric acid and 2 parts of water. The insoluble residue was mixed with water, which caused a precipitate in the acid liquid. It was mixed with the insoluble residue, the whole exhausted with æther, and then dried at 212°. The colour of the dried acid did not alter; it was yellowish-brown upon one occasion; while in another preparation it was of a pure yellow colour, like albumen. In this case, as with the latter substance, the whole was not dissolved. The water which after dilution rested above the precipitate deposited on further dilution a pale yellow sediment. This acid afforded, after being dried at 212°—

				Mean.
Carbon	50·19	50·09	50·08	50·09
Hydrogen	6·32	6·21	6·27	6·21
Nitrogen	14·47	15·03	14·78	14·77
Oxygen	26·91	26·86	27·06	27·22
Sulphur	1·71	1·71	1·71	1·71
Ash	0·10	0·10	0·10	

Solution of neutral acetate of lead furnished with one of the xanthoproteate of ammonia a yellow precipitate, which became yellowish-brown on desiccation in the water-bath. This salt, dried at 212°, afforded 14·14 per cent. oxide of lead, and for the organic substance—

	I.		II.		Mean.
Carbon.....	42·71	49·72	42·89	49·96	49·72
Hydrogen....	5·50	6·45	5·49	6·40	6·45
Nitrogen	12·63	14·69	12·63	14·69	14·69
Oxygen .... } Sulphur .... }	..	29·14	..	28·95	29·14

Xanthoproteic Acid from Fibrine.—Ox-blood is well beaten, the separated fibrine washed with water, digested for ninety-six hours with a mixture of 1 part nitric acid and 2 parts water, then mixed with water, washed, dried in the air, exhausted with æther, and dried in the water-bath. The fibrine changes its colour very slowly, with evolution of bubbles of gas. It retains its form, and very little is precipitated by water from the acid liquid. The xanthoproteic acid was of a dark brown colour. Dried at 266°, analysis afforded—

	I.	II.	Mean.
Carbon	49·22	49·39	49·31
Hydrogen	6·25	6·23	6·24
Nitrogen	14·90	14·77	14·83
Oxygen	28·26	28·24	28·25
Sulphur.....	0·94	0·94	0·94
Ash	0·43	0·43	

Xanthoproteic Acid from Horses' Hoofs.—This substance, freed from the outermost layer, was exposed to the action of 1 part nitric acid diluted with 2 parts of water for forty-eight hours, then treated as in the previous cases with water, dried in the air, and deprived of fat by digestion with æther. The form of the substance remained unaltered. Some gas was disengaged on the addition of the acid mixture. The precipitate which resulted upon the addition of water to the acid liquid was of a lighter colour than the undissolved substance, but acquired the same colour upon drying, which however was lighter than that from cow's horn. The analysis of the acid dried at 266° furnished—

	I.	II.	Mean.
Carbon	49·33	49·60	49·47
Hydrogen	6·42	6·52	6·47
Nitrogen	14·00	14·27	14·13
Oxygen	28·67	28·03	28·35
Sulphur.....	1·35	1·35	1·35
Ash	0·23	0·23	

Xanthoproteic Acid from Cheese.—Some old cheese, with the outer surface removed, was reduced to a fine powder, exhausted with æther, and then treated for forty-eight hours with a mixture of 1½ part commercial nitric acid and 2 parts water. The acid, precipitated with water, was again exhausted with æther, and thrice digested with

boiling alcohol. In the treatment with nitric acid, the cheese gave off very few bubbles of gas, remained solid, and a thick layer of fat separated on the surface, which was removed. There was no odour of valerianic acid perceptible. The colour of the pure acid was yellow, and when dried at 266° it gave—

	I.	II.	III.	Mean.
Carbon	50·82	50·63	50·54	50·66
Hydrogen	6·32	6·31	6·31	6·31
Nitrogen	14·52	14·38	14·04	14·42
Oxygen	28·20	27·54	27·97	27·78
Sulphur	0·93	0·93	0·93	0·93
Ash	0·21	0·21	0·21	

Xanthoproteic Acid from Wool.—Sheep's wool, cleansed with water and cut into small pieces, was digested for forty-eight hours with nitric acid (1 part acid and 2 water), and treated as above with water and æther, dried first in the air, and then at 266°. A few gas bubbles are disengaged on adding the acid, and the wool slowly acquires a light yellow colour. In this case some fat likewise separated. On analysing the acid dried at 266° it furnished—

			Mean.
Carbon	49·41	49·40	49·42
Hydrogen	6·50	6·35	6·42
Nitrogen	14·52	14·53	14·52
Oxygen	28·65	28·82	28·74
Sulphur	0·82	0·82	0·82
Ash	0·10	0·10	

Xanthoproteic Acid from Horn-Proteine.—Grated horn, dissolved at a gentle heat in weak solution of potash, is treated with sulphurous acid in the same manner as the albumen, and precipitated with acetic acid. The precipitate, brought upon a filter, became agglutinated into a leathery mass, which was divided as well as possible, and digested for forty-eight hours with 1 part nitric acid and 2 of water, when it entirely dissolved. The light yellow liquid was first neutralized with ammonia, then mixed with an excess of milk of lime, filtered, evaporated to the consistence of a syrup, again dissolved, filtered and precipitated with acetate of lead. The washed precipitate, dried at 266°, contained 14·00 per cent. oxide of lead, and the organic substance—

	I.		II.		Mean.
Carbon	42·90	49·89	42·91	49·94	49·91
Hydrogen	5·37	6·24	5·38	6·25	6·24
Nitrogen	12·37	14·39	12·61	16·66	14·52
Oxygen, Sulphur	..	29·48	..	29·15	29·23

The substance which remained undissolved in the first treatment with potash was digested with a fresh solution of potash, and the proteine obtained digested for forty-eight hours with 1 part nitric acid and 2 of water. In this instance only a small portion of the

substance dissolved. The insoluble residue was washed with water, digested with æther, dried at 266° and analysed; it gave—

	I.	II.	Mean.
Carbon	50·54	50·67	50·61
Hydrogen	6·41	6·42	6·41
Nitrogen	14·52	14·90	14·71
Oxygen	28·49	27·97	28·23
Sulphur	2·04	2·04	2·04

Mulder draws the following conclusions from the results of this investigation:—

1. All the so-called proteine substances furnish the same substance by treatment with nitric acid.

2. Xanthoproteic acid is nitrous acid combined with proteine; and where the latter is united with S^2O^2, this acid likewise enters into the combination. Its formula is $2C^{36}H^{26}N^4O^{12}+NO^3$.

3. In those cases where xanthoproteic acid is produced from nitric acid and proteine compounds with sulphamide, the sulphamide is decomposed, S^2O^2 is formed from it, which acid then remains in combination with NO^3 and proteine.

4. Xanthoproteic acid is a hydrate, which parts with water on combination with bases.

5. Xanthoproteic acid is not deprived of the nitrous acid by the action of chlorine.

Now since proteine unites with ClO^3, forming the compound $Pr+2ClO^3$, and xanthoproteic acid likewise enters into combination with ClO^3, Mulder is of opinion that the empiric formula for proteine, $C^{36}H^{25}N^4O^{10}+2HO$, is as firmly established as any empirical formula can be.—*Scheidk. Onderzoek.*, 5de Deel, 2de St., p. 139.

Researches on Emulsine. *By* B. W. Bull.

The emulsine employed in the following experiments was prepared from sweet almonds, from which the oil had been removed by pressure. They are formed into an emulsion with three times their weight of water, and the whole exposed for twelve hours to a temperature between 68° and 78°. In this interval a yellowish-white coagulum separates on the surface; the liquid is of a light yellow colour, and furnishes a precipitate with acetic acid, which however no longer appeared after it had been kept for two or three days. Alcohol furnishes a precipitate which entirely redissolves on the addition of water. As soon as the coagulum had separated, the liquid was filtered, and also the precipitate produced by the acetic acid. The emulsine was precipitated from the filtered solution with alcohol of 0·848 spec. grav., of which it required twice its volume.

The emulsine thus obtained, well washed with alcohol and dried in the air, is a transparent, gummy, readily-friable substance of a dark or reddish-brown colour, without odour and without any particular taste. It dissolves only after long standing or on trituration with water, leaving an insoluble residue, which contains, besides

some phosphate of magnesia and some phosphate of lime, a considerable amount of organic substance. This insoluble residue, even when completely washed with distilled water so as to remove all soluble matter, still furnishes the characteristic reaction of emulsine with amygdaline. Four analyses of this residue furnished the following results :—

	I.	II.	III.	IV.
Organic substance....	56	69·45	59·48	80·27
Ash	44	30·55	40·52	19·73

The solution of this emulsine is opalescent, and very readily converts amygdaline into oil of bitter almonds and prussic acid.

Emulsine which has been dried *in vacuo* over sulphuric acid has nearly the appearance above described; in general it is not so dark, sometimes having a brownish-yellow tint, and in other cases a brownish-red. When dried in the air, in proportion as the alcohol escapes it absorbs moisture with great avidity.

The precipitate of emulsine acquires a totally different appearance when it is first washed with strong spirit, and then with absolute alcohol, until every trace of water has been removed, and then dried *in vacuo* under sulphuric acid. It then forms a snow-white, very friable mass, which is perfectly opake, without lustre, and far more soluble than the emulsine prepared according to other methods. About 6 grms. of emulsine was obtained from a pound of almonds after the oil had been expressed. If larger quantities are employed, the time required for washing and filtration is considerably lengthened, and a more or less coloured preparation is obtained. If it is dried over sulphuric acid in a recipient filled with air, it becomes transparent, gummy and coloured by the absorption of water.

Certain substances prevent the reaction of emulsine with amygdaline, for instance alcohol and acetic acid. The property of being precipitated by alcohol is not peculiar to the emulsine, but is owing to the phosphates which it contains in solution, and with which it so intimately combined that it was impossible to separate the emulsine without destroying it.

Emulsine has an acid reaction. After it has been washed with alcohol until what passes through is perfectly neutral, the moist emulsine strongly reddens blue litmus-paper. Emulsine which has been dried and again dissolved is likewise acid, and this acid property it owes to the presence of phosphates in the almond emulsion. An emulsion of almonds, which was neutralized with lime-water and filtered, distinctly furnished the reaction with amygdaline; but the filtered liquid was not precipitated by alcohol, and it contained not a trace of phosphoric acid. Ammonia acts in the same manner. The liquid, it is true, becomes turbid on the addition of alcohol; but the turbidness cannot be removed by filtration, and is deposited only after some days as a scarcely perceptible precipitate.

When the neutralized liquid is set aside at the ordinary temperature, it begins in the course of a few days to be decomposed, with a disagreeable odour; a precipitate separates, but it no longer becomes acid.

Emulsine does not coagulate, but at a boiling heat it behaves in a very peculiar manner; between 95° and 96° its solution becomes turbid, at 113° it becomes opake and milky, and between 185° and 212° it gradually deposits a snow-white granular precipitate. If the liquid is boiled for a few minutes, the filtered solution, each time that it is heated to boiling, becomes quite opake, and deposits a copious flocculent precipitate; on cooling, this entirely redissolves. This experiment can be repeated several times with the same result. The granular precipitate first formed amounts to about 10 per cent. of the emulsine employed; it is perfectly white, can be easily reduced into a very fine powder. and leaves on incineration a neutral ash, which in one experiment amounted to 48·74, and in a second to 59·11 per cent., and consisted of phosphate of magnesia with some phosphate of lime. The organic substance combined with it contained nitrogen, but no sulphur that could be detected in it by potash and a salt of lead.

The liquid filtered from the precipitate contains two products of decomposition of emulsine, one of which, forming about a fourth of the quantity originally employed, is not precipitated by alcohol; whilst the other, constituting about 30 per cent., separates upon the addition of strong alcohol in the form of a white granular precipitate. Washed with alcohol and æther and dried, this precipitate forms a white, opake, tenacious mass, which is difficult to powder, and contains a large, although variable, amount of the above salts of phosphoric acid. Several experiments furnished from 18 to 35 per cent. of ash. The analyses gave the following results, according to which the substance differs essentially from emulsine:—

Carbon	43·17	43·11	42·48
Hydrogen	6·85	6·73	7·02
Nitrogen	8·62	8·34	8·48
Oxygen and sulphur	41·36	41·82	42·02

Acetate of lead separates this substance into two others, one of which contains sulphur, the other none. To the aqueous solution of the fresh precipitate obtained by alcohol, acetate of lead was added as long as a precipitate resulted; this was suspended in water, decomposed by sulphuretted hydrogen gas, and the excess of sulphuretted hydrogen expelled at a gentle heat. The filtered liquid had a strong acid reaction, which arose partly from phosphoric acid, partly from an organic substance. Upon concentration it formed a syrupy mass, which was decomposed by potash, with evolution of ammonia, and with a salt of lead it showed the presence of sulphur.

The liquid filtered from the precipitate obtained by acetate of lead furnished, after removing the lead and the acetic acid, on evaporation, a neutral gummy mass, readily soluble in water, and which yielded a jelly with a solution of caustic potash. It contained nitrogen, but no sulphur.

Unboiled emulsine is so completely precipitated from its solution by neutral acetate of lead, that the filtered liquid no longer furnishes oil of bitter almonds with amygdaline, whilst the lead precipitate retains this reaction.

A solution of emulsine begins, in the course of four or five days, by exposure to the air at the ordinary temperature, to be decomposed with evolution of gas; it becomes turbid; gives with neutral acetate of lead, but not with acetic acid, a copious precipitate, and still retains for some time the reaction with amygdaline.

A solution of emulsine, which has been freed from the phosphates by neutralization with lime-water, yields with neutral acetate of lead a thick precipitate. This was decomposed with sulphuretted hydrogen. After filtration and removal of the excess of sulphuretted hydrogen at a gentle heat, an acid liquid was obtained, which left on evaporation an acid gummy mass containing nitrogen. It was insoluble in alcohol and æther; it formed with baryta and silver insoluble, with magnesia soluble salts.

The liquid filtered from the precipitate with acetate of lead left on evaporation, after removing the sulphuretted hydrogen and acetic acid, a gummy nitrogenous mass.

On distilling the alcohol which had served to precipitate the emulsine, the liquid acquired a dark colour, and left on concentration an acid mass, the acid in which proved to be lactic acid.

The precipitate obtained with acetic acid previous to the precipitation of emulsine by alcohol formed, after it had been freed from fat by exhaustion with alcohol and æther, a reddish fine light powder, soluble in alkalies; but on warming the solution, it is decomposed, with disengagement of ammonia. This substance is not precipitated from its alkaline solution by alcohol; it is moreover soluble in weak, and only partially soluble in concentrated acetic acid. It contains nitrogen and sulphur, and burns with a smoky flame, leaving a small quantity of neutral ash. It dissolves in strong muriatic acid into a beautiful red liquid, which colour changes into a dark purple in the course of one or two days. It gelatinizes in sulphuric acid, and changes, with evolution of sulphurous acid, from red into black. On analysis it was found to contain 51·02 per cent. carbon, 6·87 hydrogen, 15·80 nitrogen, 25·74 oxygen, and 0·57 sulphur. The relation of nitrogen to carbon is as 1 to 7¼.

In the maceration of recently-pounded almonds with ordinary alcohol, grape-sugar was extracted, which was obtained by means of water from the residue remaining on evaporating the alcohol.

When an emulsion of almonds, prepared as above directed, is allowed to ferment for some days at about 86°, an oily coagulum separates, and the subjacent liquid becomes more and more sour. This acidification has great resemblance to the becoming sour of ordinary milk. The conversion of the sugar into lactic acid, and the union of this acid with the bases which held the caseous substance in solution, explains the separation of this coagulum and the absence of any precipitate with acetic acid, as soon as a sufficient quantity of lactic acid has been formed to separate the caseous substance from its combination with the alkalies.

Emulsine loses the property of decomposing amygdaline into oil of bitter almonds and prussic acid when its solution has been boiled,

which is not the case when it is exposed in the dry state to a temperature of 212°.

It was found very difficult to obtain the substance in a pure state fit for analysis, on which account the results do not agree very accurately with one another; however, so much is evident from the analyses, that the emulsine precipitated by alcohol has a definite composition. The materials used for the following six analyses were prepared at different times. I. to IV. were dried for several days at 212°. For No. V. a fresh emulsion of almonds was first mixed with æther to dissolve the oil, and then set aside for two or three days in a closely-stoppered vessel until the mixture had separated into two parts; the upper stratum was a thick, opake, somewhat gelatinous mass, and consisted of a solution of the oil in æther; the subjacent aqueous liquid was filtered, and immediately precipitated by alcohol. The emulsine prepared in this manner does not differ essentially in its composition from the others, as will be seen by the following numbers. VI. was prepared like I. to IV., but dried at 266°:—

	I.	II.	III.	IV.	V.	
Carbon	43·59	43·74	42·75	42·09	43·08	43·15
Hydrogen	6·96	7·33	7·37	7·34	6·81	7·39
Nitrogen.....	11·64	11·40	11·52	11·52	11·52	11·52
Sulphur	1·25	37·53	38·36	39·05	38·59	37·94
Oxygen	36·56					

The formula $C^9 H^9 NO^6$ would correspond to these numbers; and if the amount of sulphur were likewise considered essential, it would be $10(C^9 H^9 NO^6) + S$.—Liebig's *Annalen*, lxix. p. 145.

Isolation of Ethyle.

We learn that Mr. Frankland, who has for some time been pursuing his chemical studies in the laboratory of Prof. Bunsen of Marburg, has discovered ethyle, the base of æther. The isolation of this interesting base will doubtless tend to the elucidation of many involved questions connected with the phænomena of ætherification; and it must consequently prove of great interest to all chemists.—*Athenæum*, June 23, 1849.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Preparation of Vitrifiable Pigments for painting upon Porcelain. *By* H. Bohlen.

The observations recently communicated by M. Wächter on vitrifiable pigments* have induced the author to publish his experience on this subject.

* See pp. 65, 104, &c. of present volume.

Gold Purple is obtained according to the process of Lüdersdorf, by mixing a solution of 1 part ducat gold in 4 parts *aqua regia*, with 1 drm. of tin salt dissolved in 4 oz. distilled water, and a solution of 1 drm. of gum in 3 oz. of water in the following proportions:—

Distilled water	3 oz.
Solution of gum-arabic	28 grs.
Solution of tin salt	14 ...
Solution of gold	23 ...

and adding alcohol of 0·863 spec. grav. until the liquid begins to grow turbid. The purple is deposited and washed with spirit of 0·958. The dried precipitate has a brownish colour, and furnishes, when all the gum has been carefully removed by washing, a very beautiful purple after the firing.

According to Fuchs, 1 oz. *liq. ferri muriat. oxydati*, Ph. bor., is mixed with 3 oz. of distilled water and a solution of 1 oz. protochloride of tin in 6 oz. distilled water, and 10 drops of muriatic acid added until the whole has acquired a greenish colour, when a further addition of 16 oz. of distilled water is made.

On the other hand, some ducat gold is heated to boiling with pure nitric acid until all the gold is dissolved. An excess of acid should be avoided. 360 parts of distilled water are added to this solution of gold; and then the above solution of iron and tin gradually poured into it until the whole of the purple is precipitated. This precipitate has likewise a brownish tint after drying, but furnishes a beautiful purple after burning.

The author finds however that gold purple prepared according to the following process is preferable, especially as regards the external appearance:—A mixture of 4 parts pure nitric acid of 1·24 spec. grav., and 1 part pure muriatic acid which is mixed with half as much pure alcohol of 0·863, and chemically pure tin gradually added in small portions until no more is dissolved; the solution must be effected slowly, on which account the vessel containing the mixture should be placed in snow or cold water. The carefully decanted solution is diluted with 80 times its weight of distilled water, and mixed with a solution of gold prepared according to the above directions. The precipitate is purple-red, and remains so after drying. The tin solution for this purpose cannot be preserved long, otherwise nitric æther is formed; and the higher oxidation of the tin salt no longer furnishes such beautiful precipitates with gold as the recently prepared solution.

For mixing with the purple in order to produce a rose colour, the author does not employ carbonate of silver, but the metal in a very minute state of division obtained by mixing the finest silver leaf with honey and a few drops of æther, and well grinding it, when the honey is washed out with water. The author uses as a flux for the purple colours a lead glass consisting of 6 parts minium, 2 parts silica and 2 parts of calcined borax.

With respect to the *chrome colours*, the author observes that the expensive method for their preparation by means of the chromate

of the protoxide of mercury is still the only one by means of which a fine colour can be obtained.

Cobalt Colours.—In purifying the cobalt for porcelain colours, the removal of the whole of the arsenic is of less consequence than that of the iron. Cobalt ores from various localities, Tunaberg, Saxony and Thuringia, are treated in the following manner. The mineral is reduced to a fine powder in an iron mortar kept for the purpose, and mixed with one-fifth its weight of charcoal powder; then exposed in Hessian crucibles to a red heat under a chimney with a good draught or in the open air, and roasted as long as arsenical vapours escape,—a very disagreeable operation, which lasts several hours. The ore thus prepared is now boiled over the fire with a mixture of 4 parts nitric and 1 part muriatic acids, 1 part of which is diluted with 3 parts of water. This operation is repeated about three times with less acid. The liquids are allowed to settle, the clear portion decanted, the remainder diluted with water and filtered, and the solution evaporated to dryness. The dry mass is mixed with some water, heated, and separated by filtration from the residue of arseniate of iron. The green liquid, which now contains more or less cobalt, iron, nickel and manganese, is mixed with a filtered solution of pearlash until the dirty reddish precipitate begins to turn blue. Care and experience in this operation are requisite, otherwise a loss of cobalt might result. The precipitate of arseniate and carbonate of iron, which at the same time contains nickel and manganese, is separated by filtration, and the beautiful red liquid mixed with more of the solution of pearlash until the whole of the cobalt is precipitated; the precipitate is carefully washed and dried. This hydrated oxide of cobalt is sufficiently pure for technical purposes, and answers just as well as that prepared from oxalate of cobalt or by caustic ammonia.

For painting, the oxide of cobalt is heated in a Hessian crucible with 1 part silica and $1\frac{1}{2}$ part oxide of zinc for two hours in a blast furnace, then reduced to a fine powder in a porcelain mortar, and mixed with an equal weight of lead glass.

Yellow Colours.—A beautiful yellow is obtained from 2 oz. minium, $\frac{1}{2}$ an oz. *Stib. oxydat. alb. abl.*, 2 drms. oxide of zinc, 2 drms. 2 scruples calcined borax, $\frac{1}{2}$ an oz. silica, $\frac{1}{2}$ a drm. dry carbonate of soda, and 1 scruple *ferr. oxydat. fuscum*, which are well mixed, fused in a crucible, and then ground fine.—*Archiv der Pharm.*, lvii. p. 276.

On a new Method for amalgamating Zinc.
By Prof. O. N. Stoddard.

This method consists in the employment of double chloride of zinc and ammonia (the same solution which is so useful in soldering iron and steel).

The zinc to be amalgamated is heated to about 450° or 500° F., and the liquid applied by a cloth or sponge, and the mercury suffered to flow immediately over the surface while still moist.

The union is instantaneous and complete, and the depth of the amalgamation is easily regulated by the quantity of mercury suffered to remain in contact with the zinc.

This method is applicable even when the zinc is thoroughly oxidized on the surface; but if it has been previously used in a galvanic battery, it is best to cleanse the surface first by immersion in somewhat concentrated hydrochloric acid.

A set of Grove's cylinders thus amalgamated, it is stated, have been used at Miami University during a long course of lectures without serious injury and without reamalgamation.—Silliman's *Journal*, May 1849.

New Process for the Manufacture of Sulphate of Soda.

We learn from the 'Comptes Rendus' of the 5th of February, that Messrs. Thomas, Dellisse and Boucard, civil engineers, have presented to the Academy the description of a new process for converting culinary salt into sulphate of soda by means of the sulphate of iron. This would allow the pyrites to be turned to very good account. The dry and pure sulphate of soda would not cost more than $2\frac{1}{2}$ francs the 100 kilogrammes instead of 12 to 18 francs, which is the ordinary price. The new process would moreover avoid all the disadvantages attending the production of the vapours of muriatic acid.

PROCEEDINGS OF SOCIETIES.

Royal Society.

March 29, 1849.

(George Rennie, Esq., Treasurer, Vice-President, in the Chair.)

"Examination of the Proximate Principles of some of the Lichens."—Part II. By John Stenhouse, Esq., F.R.S.

Gyrophora pustulata.

The author states that this lichen, which is the "Tripe de Roche" of the Canadian hunters, has been long employed by the manufacturers of archil, though the quantity of colouring matter contained in it is by no means considerable, being little more than a twelfth of that in the *Roccella Montagnei*. The *Gyrophora pustulata*, on which the author operated, was brought from Norway, where it is annually collected in considerable quantity for the manufacture of archil. The colouring principle was extracted by maceration with milk of lime, and was precipitated in a gelatinous state by neutralizing the lime solution by muriatic acid precisely in the way so frequently described in the author's former paper (Phil. Trans. 1848). The precipitate was gently dried, and then dissolved in hot spirits of wine. On the cooling of the liquid, the colouring principle was deposited in small soft crystals, which by digestion with animal charcoal and repeated crystallizations were rendered quite colour-

less. This principle, to which the author has given the name of *Gyrophoric acid,* is almost insoluble in either hot or cold water, and is also much less soluble in hot spirits of wine than either orsellic, erythric, or any of the analogous colouring principles. It is neutral to test-paper, and possesses no saturating power, as the smallest quantity of an alkali gives its solutions an alkaline reaction. Gyrophoric acid strikes a bright red fugitive colour with hypochlorite of lime; and when macerated with a solution of ammonia, it is slowly converted into a purplish-red colouring matter, similar to that yielded by the analogous acids under the same circumstances. When subjected to analysis, the formula of gyrophoric acid was found to be $C_{36}H_{18}O_{15}$.

Gyrophoric acid when boiled for some hours in alcohol yields an ether similar in appearance and properties to the erythric and lecanoric ethers; its formula is $C_4H_5O+C_{36}H_{18}O_{15}$.

Gyrophoric acid unites with the alkalies and metallic oxides, but the compounds which it forms possess little stability and cannot be procured of an uniform composition.

Lecanora tartarea.

This lichen, like the *Gyrophora pustulata,* has been employed from an early period in the manufacture of archil. It is found in considerable abundance in the hilly districts of the northern parts both of Scotland and Ireland. The lichen on which the author operated came from Norway. He found it also to contain gyrophoric acid, in much about the same quantity as the *Gyrophora pustulata.* This fact was established by the analysis of the acid itself and of its ether compound.

Brom-orcine.

In the author's former paper on the proximate principles of the lichens, read before the Royal Society on the 3rd of February 1848, he described a crystalline body obtained by cautiously adding bromine to an aqueous solution of orcine. In this second part he states that, in the 'Comptes Rendus' for August of the same year, Messrs. Laurent and Gerhardt describe the very same compound obtained in precisely the same way, without even hinting that it had been previously discovered. These gentlemen however give a different formula for the compound, viz. $C_{14}H_5Br_3O_4$, or orcine in which three equivalents of hydrogen are replaced by three equivalents of bromine; and the author is disposed to adopt this formula, as, on repeating the analysis of the compound, he found that he had somewhat over-estimated the amount of bromine contained in it, while its other constituents were determined correctly enough.

Beta-orcine.

This substance, described by the author in the Philosophical Magazine for July 1848, may be obtained from usnic acid, either by destructively distilling it, or by acting on it with alkalies.

Beta-orcine crystallizes very beautifully in four-sided prisms surmounted at either end by four-sided pyramids. These crystals have a brilliant lustre, and are from three quarters of an inch to an inch

long. Their solution strikes a fugitive bright-red colour with hypochlorite of lime, and with a solution of ammonia it yields a permanent blood-red colouring matter which becomes darker on standing. The formula of beta-orcine, which however is merely empirical, is $C_{16} H_{10} O_4$.

Quintonitrated erythromannite.

In his former paper on the lichens, the author has described, under the name of *pseudo-orcine*, a remarkably beautiful crystalline body which is obtained by boiling either picro-erythrine, or erythric acid, with an excess of lime or baryta. This substance he then regarded as very analogous to mannite both in its composition and properties, and this view having been amply verified by an experiment which he has recently made, he has been induced to change the name of this compound to *erythro-mannite*, as at once indicating its origin and its most striking properties. After referring to the discovery by Messrs. Flores Domonte and Menard, of "Mannite quintonitrique" or mannite in which five equivalents of water are replaced by five equivalents of nitric acid, and which possesses the remarkable property of detonating so violently when struck by a hammer that M. Sobrero has proposed employing it, instead of fulminate of mercury, in the manufacture of percussion-caps, the author states that when erythro-mannite is treated with fuming nitric acid, in exactly the same way as mannite, it yields a perfectly analogous compound, or erythro-mannite in which five equivalents of water are replaced by five equivalents of nitric acid. This compound, which he has called *quintonitrated erythromannite*, is also insoluble in water, but crystallizes out of hot spirits in large flat crystals resembling those of benzoic acid, only larger and exhibiting a much more pearly lustre. Quintonitrated erythromannite also detonates with great violence when it is mixed with a little dry sand, and is strongly struck with a hammer.

In order to exhibit more distinctly the close analogy which subsists between the four compounds, their rational formulæ are given, viz.

Mannite ..... $= C_{12} H_{14} O_{12}$;
Erythro-mannite ..... $= C_{11} H_{14} O_{11}$;
Quintonitrated mannite ..... $= C_{12} H_9 O_7 + 5NO_5$;
Quintonitrated erythromannite $= C_{11} H_9 O_6 + 5NO_5$.

May 24, 1849.

(The Earl of Rosse, President, in the Chair.)

An appendix to a paper "On the Variations of the Acidity of the Urine in the State of Health"—"On the Influence of Medicines on the Acidity of the Urine." By Henry Bence Jones, M.D., M.A., F.R.S. &c.

The variations of the acidity of the urine in the state of health having been shown in the original paper, and the effect of dilute sulphuric acid also traced; in this appendix the influence of caustic potash, of tartaric acid, and of tartrate of soda, on the acidity of the urine is determined.

One ounce of liquor potassæ, specific gravity 1072, was taken in distilled water, in three days. It hindered the acidity of the urine from rising long after digestion to the height to which (from comparative experiments) it otherwise would have done; but it by no means made the urine constantly alkaline; nor did it hinder the variations produced by the state of the stomach from being very evident.

354 grains of dry and pure tartaric acid dissolved in water were taken in three days. The conclusion from the observations is that this quantity increased the acidity of the urine, but during that time it did not render the effect of the stomach on the reaction of the urine less apparent than when no acid was taken; and therefore, that this quantity of tartaric acid, during this time, does not produce so much effect on the reaction of the urine as the stomach does.

Tartrate of potash in large doses produces the most marked effect on the alkalescence of the urine. 120 grains of pure dry tartrate of potash dissolved in four ounces of distilled water made the urine alkaline in thirty-five minutes. In two hours the alkalescence had disappeared, but after the next meal the effect of the tartrate of potash was again apparent. 10 drachms of tartrate of potash taken in three days produced but little, if any effect, on the acidity of the urine twenty-four hours after the last dose was taken.

June 14, 1849.

(The Earl of Rosse, President, in the Chair.)

"On Carbonate of Lime as an ingredient of Sea Water." By John Davy, M.D., F.R.S. Lond. & Ed., Inspector General of Army Hospitals, &c.

Considering the manner in which cliffs consisting of limestone are worn away by sea water in situations not favourable to the disengagement of carbonic acid gas; and on the other hand, the manner in which sand is consolidated and converted into sandstone in other situations favourable to the disengagement of this acid gas, and the deposition of carbonate of lime (the cementing principle) in consequence, the author has been induced to make trials of the water of the ocean, in crossing the Atlantic, to endeavour to ascertain whether carbonate of lime is widely diffused through the waters of the ocean, or is chiefly an ingredient of sea water at no great distance from land.

The results of his experiments have been of a negative kind, seeming to show that carbonate of lime exists principally in seas, where its presence is most easily accounted for, and where in the economy of nature, it may be supposed, it is most useful.

The author describes also some trials which he made on sea water in relation to the sulphate of lime it contains, which he found to be variable in quantity in different situations. He suggests the propriety of having further and more extended inquiry made on this point, believing that the results may be important in connexion with steam navigation,—the injurious incrustation which is liable to form on the inside of the boilers of steam vessels at sea, being composed chiefly of this compound.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Peucedanine. By Dr. F. Bote.

This substance, which was discovered by Schlatter, and more accurately examined by Erdmann, is best obtained by digesting the root of *Peucedanum officinale* cut into small pieces with alcohol of 0·833 spec. grav. for several hours, and then heating it with the liquid to boiling. The filtered liquid furnishes, after being slightly evaporated, crystals of peucedanine, which are freed by means of very dilute cold alcohol, in which they are very sparingly soluble, from a brown resinous mass. The crystalline mass obtained from the subsequent extracts contains far more of the smeary substance than the first, and it is not advisable to mix the several extracts and treat them in one operation. When a dilute alcohol is employed for the first extract, the produce is never so great as according to the method directed. That portion of peucedanine which the last traces of resin contain may still be obtained by diluting the hot alcoholic solution with water so long as the turbidness produced disappears by agitation and a gentle heat. After long standing, the cold liquid deposits some crystals, which are obtained perfectly pure by repeated solution in cold æther and crystallization. The small residue insoluble in the cold æther consists of Erdmann's *oxypeucedanine*.

Peucedanine, $C^{24}H^{12}O^{6}$, forms, when crystallized from æther, shining colourless prisms, which belong to the rhombic system. The crystals melt at 167° without any loss of weight; the fused mass turns brown at 266°, and a slight sublimation takes place. The most simple relation between the constituents may be expressed according to the following analysis by $C^{4}H^{2}O$:—

Carbon.....	70·45	70·52	4	70·59
Hydrogen	5·92	5·98	2	5·89
Oxygen	23·63	22·77	1	23·52

The above formula, although not so simple, appears to be the correct one, notwithstanding that it was impossible to prepare a combination of peucedanine with bases.

Oxypeucedanine, which has already been noticed by Erdmann, and which differs from peucedanine by its insolubility in cold æther and a higher melting-point, has, according to the author, the composition $C^{24}H^{11}O^{7}$.

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It is formed when apparently pure peucedanine is dissolved in cold æther, when it is left behind as a granular residue, which can be freed from adherent peucedanine, although with difficulty, by frequent crystallization and treatment with cold æther. The highest melting-point which the most purified substance presented was 291°. The substance was then considered to be pure, and analysed; the following numbers were obtained:—

Carbon	68·13	67·95	24	68·25
Hydrogen	5·35	5·38	11	5·21
Oxygen	26·52	26·67	7	26·54

Nitropeucedanine, $C^{24}H^{10}NO^9$, is obtained by heating peucedanine with nitric acid of 1·21 spec. grav. to about 140°; the peucedanine dissolves slowly but entirely, imparting to the liquid a yellow colour. On cooling, the liquid solidifies to a laminar crystalline mass, which may easily be obtained pure by filtration and solution in alcohol. In this state it forms colourless, flexible, crystalline laminæ, which are pretty readily soluble in alcohol and æther, and are nearly insoluble in water. At 212° the substance remains unaltered; at a higher temperature it fuses, and is at the same time decomposed; it burns on platinum foil with a smoky luminous flame, like peucedanine, but with evolution of nitrous acid vapours. Its behaviour towards acids and bases is not very characteristic; strong agents decompose it. It furnished on analysis—

Carbon	60·06	60·02	24	60·00
Hydrogen	4·21	4·20	10	4·16
Nitrogen	5·50	5·95	1	5·83
Oxygen	30·23	29·83	9	30·01

In the treatment of peucedanine with nitric acid, Erdmann's oxypicric acid and large quantities of oxalic acid are frequently obtained as collateral products. With respect to the first, all the properties of the acid obtained from peucedanine agree with those described by Erdmann and by Will and Böttiger.

Nitropeucedaninamide, $C^{24}H^{12}N^2O^8$, is obtained by exposing nitropeucedanine in a current of ammoniacal gas at 212°. It increases in weight, and is finally wholly converted into the new substance. The product obtained directly in this reaction dissolves pretty readily in boiling alcohol, and crystallizes on cooling in rhombic prisms, which have almost a diamond lustre. It is equally obtained, only less readily and pure, by heating peucedanine with ammonia and alcohol.

Nitropeucedaninamide is not decomposed by weak acids in the cold, but is so on the application of heat; the liquid then contains nitropeucedanine and the ammonia salt of the acid employed. On treatment with strong bases, it exhibits the character of an amidogen compound by slowly giving off ammonia on ebullition. It is readily soluble in alcohol and æther, but almost insoluble in water. This last circumstance gives rise to a very interesting reaction. If an alcoholic solution be diluted with water, the substance slowly

separates, and the very slightly turbid liquid exhibits the phænomenon of dichroism in a remarkable degree. The appearance is most striking when nitropeucedaninamide containing some oxypicric acid is mixed with a solution of ammonia; the liquid is then yellow by transmitted light, and of a beautiful azure-blue by reflected light, which last colour is still distinctly perceptible with the greatest dilution. This reaction furnishes a means of discovering the smallest quantity of nitropeucedaninamide, and consequently also of nitropeucedanine and peucedanine. On analysis, nitropeucedaninamide furnished—

Carbon	57·85	24	58·06
Hydrogen	4·89	12	4·83
Nitrogen	11·09	2	11·29
Oxygen	26·17	8	25·92

Journ. für Prakt. Chem., xlvi. p. 371.

On the Atomic Weight of Silica. By H. Kopp.

The doubts entertained respecting the atomic weight of silicon and the composition of silica according to one of the three formulæ SiO, SiO^2 or SiO^3, have not been solved by the views which have hitherto prevailed on this subject, where in general the decision has been made to depend on the circumstance, that a particular series of compounds might be most simply represented, sometimes according to one, sometimes according to the other formula. A peculiar mode of conceiving this subject shows that, admitting the correctness of the analytical results of Pelouze, the atomic weight of silicon with H=1 is 21·3, and the formula of silicic acid SiO^3.

Kopp has deduced this result from the difference between the boiling-points of the chromide and bromide of silicon. The possibility of deciding the question by this means is sufficiently evident from a number of determinations of the differences between the boiling-points of several chlorides and bromides, in which the chlorine, on the one hand, may be regarded as a substitute for the bromine in the otherwise corresponding bromide, thereby establishing how many degrees the boiling-point rises or falls when in any compound chlorine is replaced by bromine, or *vice versâ* bromine by chlorine. After establishing the number of degrees which express this difference for the substitution of each atom of chlorine or bromine, it is possible, on the other hand, to conclude, from the difference between the boiling-points of a chloride and the corresponding bromide, as to the number of atoms replaced. Now it results, from the comparison of the boiling-points of several bromides and chlorides, that the substitution of 1 Cl by 1 Br raises the boiling-point 32° Cent. of 2 Cl by 2 Br $2 \times 32 = 64°$ of 3 Cl by 3 B $3 \times 32 = 96°$, while the boiling-point falls in the same proportion when, on the contrary, bromine is replaced by chlorine. Compare, for example, the boiling-point of the following substances:—

		Boiling-point.
$C^4 H^5 Cl$....	Chlorethyle	+11°, Pierre.
$C^4 H^3 Cl$....	Chloracetyle	−18° to 15°, Regnault.
PCl^3	Chloride of phosphorus....	78°, Dumas, Pierre.

		Boiling-point found.	Calculated.
$C^4 H^5 Br$....	Bromethyle	41° Pierre....	43°.
$C^4 H^3 Br$....	Bromacetyle	Ord. temp....	14° to 17°.
PBr^3	Bromide of phosphorus....	175°, Pierre ..	174°.

Several other comparisons enumerated by Kopp lead to the law above announced respecting the change in the boiling-point in substitutions of bromine and chlorine. It consequently follows, as above stated, that according as the boiling-point of a bromide, on comparison with that of its corresponding chloride, is situated at 32, 64 or 96 degrees higher than in the chlorine compound, this latter must be regarded as containing 1, 2, 3 atoms of chlorine replaced by bromine. The boiling-points of the chloride of silicon and of the bromide of silicon have been determined by Pierre, a most accurate observer, the first to be 59°, the latter to be 153°; the difference is 94°; whence it follows that in the bromide of silicon 3 atoms of bromine are substituted for 3 atoms of chlorine in the chloride of silicon; that the first is $SiBr^3$, the latter $SiCl^3$, and that silica is therefore SiO^3; and consequently we must admit the atomic weight of silicon to be 21·3, H being assumed =1.—Liebig's *Annalen*, lxvii. p. 356.

On the Constitution of Styracine. *By* Dr. A. Strecker.

The interesting investigation of M. Toel* has made us acquainted with a body which is well suited to excite our interest in a high degree. A certain analogy in the constitution of styracine with the natural fats is clearly proved, and merits our attention the more as no acid corresponding to cinnamic acid has hitherto been detected in nature in such conjugate union; nor, with the exception of the alcohols belonging to the series $C^{2n} H^{2(n+1)} O^2$, which correspond to the acids $C^{2n} H^{2n} O^4$, was even the occurrence of glycerine in analogous combinations known. The conjugate glycerine compounds of the fatty acids which occur in nature appear however to differ, as was already pointed out by Gerhardt, from the conjugate alcoholic compounds, as well as from the artificially prepared glycerine compounds, in their being decomposed, with the absorption of *six* equivalents water, into 2 equivs. acid and 1 equiv. glycerine ($C^6 H^8 O^6$), although this cannot be considered as firmly established from the difficulties which occur in obtaining these compounds pure, and which is increased by their generally high atomic weights. They would differ from the neutral æthers in the latter furnishing on decomposition only 1 equiv. acid to 1 equiv. alcohol, with assimilation of 2 equivs. water. The artificial glycerine compounds, which all correspond to the acid æthers, furnish like these 2 equivs. acid and 1 equiv. glycerine, with assimilation of 2 equivs. water.

* Page 249 of the present volume.

Considered from this point of view, styracine, although approaching closely to the fats, appears to stand in a more intimate relation with the conjugate alcoholic compounds, among which must be included spermaceti and, according to Brodie's investigation, one constituent of wax.

In fact, the formula of styrone advanced by M. Toel has not been further checked by a determination of its atomic weight; and we may therefore advance for this body other formulæ, which likewise agree with the composition found. Now I believe to have succeeded in finding a formula for styrone, which has the property, in common with that of M. Toel, of accounting for the composition of the compounds, but deserves the preference from its greater simplicity. I assign to styrone the formula $C^{18} H^{10} O^2$, which requires in 100 parts—

	Calculated.	Found.	Toel.	
Carbon	80·62	79·8	80·2	80·6
Hydrogen	7·45	7·6	7·7	7·6
Oxygen	11·93	12·6	12·2	11·8

The analyses agree, as to the amount of hydrogen, better with my formula than with M. Toel's.

According to this the composition of styracine becomes—

1 equiv. cinnamic acid	$C^{18} H^8 O^4$
1 equiv. styrone	$C^{18} H^{10} O^2$
	$C^{36} H^{18} O^6$
—2 equivs. water	$H^2 O^2$
1 equiv. styracine	$C^{36} H^{16} O^4$

and the per-centage composition—

	Calculated.	Found.	Toel.	
Carbon.....	81·85	82·56	82·57	82·61 82·15
Hydrogen ..	6·02	6·12	6·49	6·36 6·16
Oxygen	12·13	11·32	10·94	11·03 11·69

The amount of carbon found is considerably higher than the calculated quantity; but it is well known that this is not impossible in combustions in oxygen gas; on the other hand, the loss in hydrogen, according to the other formula, is avoided by the present one.

The formula of chlorostyracine becomes $C^{36} H^{12} Cl^4 O^4$, and its composition—

	Calculated.	Found.	
Carbon	53·79	53·64	
Hydrogen	3·00		
Chlorine.....	35·27	35·40	35·60
Oxygen	7·94		

Styrone might perhaps be regarded as the hydrate of an oxide ($C^{18} H^9$), and its constitution would then be represented by $(C^{18} H^9) O + HO$.

Laying aside all theoretical considerations which may be entertained respecting the alcohols, styrone stands, according to the above formula, in a similar relation to cinnamic acid as vinous alcohol to acetic acid, ethal to cetic acid (ethalic acid), &c.; or, to express it in a few words, *styrone is the alcohol of cinnamic acid.* Styrone $=C^{18}H^{10}O^{2}-H^{2}+O^{2}=C^{18}H^{8}O^{4}$=cinnamic acid. As is seen, styrone contains 2 equivs. hydrogen more and 2 equivs. oxygen less than cinnamic acid, precisely as is the case with all the other known alcohols.—Liebig's *Annalen*, April 1849.

On Pectic Acid from Pine Wood. By M. Sacc.

According to the author, pine wood consists of insoluble pectic acid, and of another substance which is very probably lignose, and which by oxidation and absorption of water may be converted into soluble pectic acid. When pine wood is treated with nitric acid, it is partially converted into pectic acid. When pectic acid is converted in the interior of plants into cellulose, or any other amylaceous substance, there are formed at the same time cane-sugar, carbonic acid and water. The pectic acid is the substratum of all these vegetable substances, as the amylaceous principles are derived from it. The author's pectic acid is represented by the formula $C^{14}H^{12}O^{13}$. [These statements however are scarcely borne out by the facts contained in the author's paper.]

The wood of *Abies pectinata*, of moderate size, grown in the neighbourhood of the village Rochefort, Neufchatel, was boiled with ordinary nitric acid (200 grms. of wood dried at 212°, 400 grms. water, and 4 lbs. of acid) until it was converted into a pasty mass; it was then filtered through fragments of glass; the filtered liquid contained somewhat more than 15 grms. of oxalic acid; the residue was washed for a long time with water on the funnel, and finally collected on a cloth and well pressed. In this state the substance does not dissolve in water; but with 3 to 4 times its volume of water and a little ammonia, swells up, becomes transparent, and forms a solution, from which the weakest acids precipitate the entire mass as a colourless transparent jelly, which is so thick that the vessel containing it may be turned upside down without anything falling out. According to the author, this substance is pectic acid. It still contained 0·595 per cent. ash, and on analysis gave—

Carbon	40·83	42·10	42·86	14	42
Hydrogen	5·86	6·00	5·94	12	6
Oxygen	53·31	51·90	51·20	13	52

This pectic acid, when once dried at 212°, becomes insoluble in water and in ammoniacal water. Pine wood is represented, according to the author, by $C^{21}H^{17}O^{15}$. Subtracting pectic acid from it, there remain $C^{7}H^{5}O^{2}$; doubling this, adding 7O and 2HO, we have again $C^{14}H^{12}O^{13}$; that is to say, 2 equivs. pine wood may be converted into 3 equivs. pectic acid by the absorption of 7 atoms oxygen and 2 of water.

The author has also analysed the ashes of the pine wood which he examined. The thin shavings contained about 38 per cent. of water and 62 per cent. woody substance (*ligneux*); the latter furnished 0·5538 per cent. ash, which consisted in 100 parts of—

Silica	10·8667
Sulphuric acid	1·2844
Phosphoric acid	3·5569
Chlorine	0·1229
Peroxide of iron	2·6018
Protoxide of manganese	2·6498
Magnesia	3·9873
Lime	58·6475
Potash	2·3076
Soda	13·9751

Ann. de Chim. et de Phys., xxv. p. 219.

On the Specific Heat of Potassium. By V. Regnault.

Dulong and Petit discovered that between the specific heats of simple bodies and their chemical equivalents the following law existed:—*The specific heats of the simple bodies are in inverse proportion to their atomic weights.* Among the small number of numerical results which these illustrious philosophers brought forward in support of their law, there were several which satisfied this relation; but these atomic weights were subsequently found to be quite inaccurate. The anomalies which existed in the law of Dulong and Petit have for a long time led chemists not to use it in fixing the equivalents of substances which they could not succeed in establishing in a certain manner by purely chemical data. In my memoir on the specific heat of simple bodies, I have shown that the anomalies detected in the law of Dulong and Petit were owing to the very inaccurate determinations of several of their specific heats; but at the same time I observed that this law did not possess the degree of accuracy which they supposed, and that it was merely approximative. This is owing to the circumstance that the calorific capacity of bodies, as we obtain it by our experiments, contains several other elements, which it has hitherto not been possible to separate, in particular the latent heat of expansion and a portion of the latent heat of fusion, which the substances successively absorb in proportion as they soften, frequently long before the temperature considered as their melting-point. The changes which have for some time past been made in the numerical value of the equivalents of some of the simple bodies have in general diminished the differences which I had pointed out in my first memoir.

Nevertheless, among the large number of simple substances whose specific heats I was able to determine, there are still three which do not come within the law, unless the equivalents generally adopted by chemists are changed; these bodies are uranium, silver and carbon.

Uranium exhibited an inexplicable anomaly, which led me to induce chemists to make this body the subject of further research. Shortly afterwards the beautiful experiments of M. Peligot showed that the substance hitherto regarded as metallic uranium was an oxide; and this able chemist succeeded in isolating from it the true metal.

With respect to silver, the law of the specific heats assigned to this metal an equivalent half of that generally adopted by chemists. The formula for oxide of silver ought consequently not to be written AgO but Ag^2O; it became similar to that of the protoxide of copper, Cu^2O, and of the protoxide of mercury, Hg^2O. I pointed out the reasons which should lead chemists to adopt this new equivalent for silver, especially the undoubted isomorphism of the sulphuret of silver with the sulphuret of copper, Cu^2S, which it replaces in every proportion in some crystalline minerals; the analogy of the chloride of silver with the chloride of copper, Cu^2Cl, and this circumstance, that no salt of silver had ever been met with which was isomorphous with the corresponding salt formed by an oxide of the formula RO. These reasons appear so conclusive to me, that I have no doubt chemists will soon adopt the equivalent of silver as deduced from the specific heat of that metal.

Carbon exists free in several states, and then exhibits very distinct physical properties. I have shown that very different specific heats correspond to these several states. It must be determined in what state the carbon enters into its chemical combinations; and it is evidently that the specific heat of which is in relation to the equivalent. It is natural to suppose that it is that modification in which the carbon is most divided. Now the calorific capacity which I found for a carbon derived from the decomposition of organic substances by heat corresponds to the equivalent 150, that is to say, to a number twice that of 75 admitted by the majority of chemists. I enumerated the reasons which gave great probability to the accuracy of this new equivalent for carbon; among them there is one which appears to me to be decisive. We are at present acquainted with a very large number of substances derived from the organic kingdom, the composition of which is established with certainty; *all* their formulæ exhibit this remarkable peculiarity, *that the number of the equivalents of the carbon is an even number*. Now this fact is quite natural if the equivalent admitted by chemists is the half of the true equivalent; the sole exceptions are formed by two combinations of carbon, which serve to fix the old equivalent of this body, viz. the oxide of carbon and carbonic acid; but there is no reason why we should write the formula of the oxide of carbon CO rather than C^2O^2; and with respect to carbonic acid, chemists write its formula CO^2, because they regard as neutral carbonates those which most commonly occur, as the carbonates of lime, of baryta, &c., and as bicarbonates the alkaline carbonates, which contain twice the amount of carbonic acid. The anomaly presented by carbonic acid disappears, if, on the contrary, these last salts are viewed as neutral carbonates, as several chemists have maintained to the present time.

The carbonates containing a less amount of carbonic acid, thus become basic, or subcarbonates.

There exists between the specific heats of compound bodies a law analogous to that just alluded to for the simple bodies, and which has proved to be true within the same limits. This law is as follows:—*The specific heats of compound bodies presenting the same chemical formulæ are reciprocally in inverse proportion to their equivalents.* However, my experiments prove that, for this law to be general, some of the equivalents admitted by chemists must be modified.

The compounds of silver, the formulæ of which, when the oxide is written AgO, are similar to those of the corresponding compounds furnished by the oxides RO, constantly form exceptions to the law. But if the oxide of silver is written Ag^2O, its salts, compared with those formed by the protoxides Cu^2O, Hg^2O, which then have analogous formulæ, satisfy the law of specific heats; and the same applies to the binary compounds. The specific heats of the compounds of silver, as likewise that of metallic silver, lead therefore to the same conclusion, viz. *that we must adopt for silver an equivalent half that admitted by chemists.*

My experiments have also placed in evidence another fact, which deserves attention. The formulæ KO and NaO are generally admitted for potash and soda. These bases thus present similar formulæ to those of baryta, lime, magnesia, the protoxides of iron and of lead, &c. If we adopt these formulæ for the alkaline oxides, the specific heats of their salts and those of the binary compounds of the alkaline metals form exceptions to the law of specific heats. But if we write the formulæ of the alkaline oxides K^2O, Na^2O, the anomaly disappears. These bases then become isomorphous with the protoxide of copper Cu^2O, with the protoxide of mercury Hg^2O, and with the oxide of silver supposing its formula to be written Ag^2O. In my memoir on the specific heat of compound bodies, I have exposed the reasons which should induce chemists to adopt this change. The following are the principal:—No alkaline salt is known which is isomorphous with the corresponding salt formed by an oxide RO; and the oxides of the alkalies never replace in indefinite proportions an oxide of the formula RO. Mineralogists, it is true, frequently admit these substitutions, which facilitate the establishment of their formulæ; but it is a gratuitous hypothesis, which has already been abandoned with regard to several minerals as soon as their composition was better known. Lastly, according to Mitscherlich, the sulphate of silver presents the same crystalline form as the anhydrous sulphate of soda.

To complete this determination of the equivalents of the alkaline metals, it became very desirable to obtain the specific heat of potassium. I have endeavoured to determine it several times, but have always met with great difficulties; in the first place, it is difficult to obtain potassium in a pure state, and to experiment with it in contact with the air without its being altered; and then its specific heat

cannot be determined above 32°, because the metal softens and contains a considerable amount of its latent heat of fusion. I have succeeded in determining the specific heat of potassium in a very approximate manner, by cooling this metal in solid carbonic acid, and ascertaining the decrease of temperature which it produced upon a certain quantity of naphtha contained in a small calorimeter. By making a perfectly similar experiment upon a known weight of lead, I was able to determine the relation between the specific heats of potassium and lead considered under the same circumstances of temperature. Three experiments have given the following values —5·83, 5·77, 5·40.

The two first values are too great, because I was not able to prevent in my two experiments the ingot of potassium carrying with it the small quantity of solid carbonic acid which adhered to its sides, and produced too great a decrease of temperature. Now the inverse relation of the atomic weights adopted by chemists is $\frac{1294{\cdot}5}{490{\cdot}0} = 2{\cdot}64$, that is to say, very nearly half the relation of the specific heats found in my experiments. If, on the contrary, the equivalent which I propose is adopted, this relation becomes $\frac{1294{\cdot}5}{245{\cdot}0} = 5{\cdot}29$, which differs very slightly from the relation of the specific heats given by the third and most accurate experiment. The specific heat of potassium leads consequently to the conclusion which I had arrived at from the specific heats of the compounds of this metal, viz. *that the equivalent of potassium should be doubled, and that the formulæ of the alkaline oxides should be written* R^2O.

I have endeavoured to demonstrate by some direct experiments, that the method which I have followed for the determination of the specific heat of potassium is not liable to very great error. With this view I employed it in determining the specific heat of two bodies, the calorific conductibility of which is considerably weaker than that of potassium, for instance phosphorus and ice. The experiment was made in the same way as for the potassium, merely substituting water for the naphtha in the calorimeter. Admitting for the specific heat of lead between −108° and 32° the same number, 0·0314, which I found for this metal between 32° and 212° (a supposition which probably differs but very slightly from truth), I found for the specific heat of phosphorus—

Between −108° and +50°	0·1740
M. Person found between −5°·8 and +44°·6....	0·1788
I found between +50° and +86°	0·1887

In the last case the phosphorus had become perceptibly soft. From these experiments it is seen that the specific heat which I have found for the phosphorus at these low temperatures is that which would have been supposed *à priori*, on admitting that the calorific capacity of this substance diminishes with the temperature.

The specific heat of ice between −108° and 32° I found to be

0·474 ; Person and Desains both found 0·504 between −4° and 32°, *i. e.* a number somewhat higher than I found; but this should be the case, as the specific heat determined in my experiment refers to much lower temperatures.—*Comptes Rendus*, xxviii. p. 326.

On the Amount of Lime in Lime-Water. By M. Wittstein.

According to the author, 732 parts of cold water dissolve 1 part of anhydrous lime. The experiments to determine the solubility of lime in boiling water did not afford a satisfactory result; three experiments gave 1495, 1570 and 1311 parts of boiling water to 1 part of anhydrous lime. The carbonate of lime which separates from lime-water on exposure to the air is the neutral carbonate, CaO, CO^2.—Buchner's *Repert.*, i. p. 182.

On the Crystallized Hydrate of Sulphuric Acid.
By Prof. Wackenroder.

The author observes, with respect to the application recently proposed by Hayes*, of the crystallized hydrate of sulphuric acid, SO^3 2HO, for the preparation of pure sulphuric acid, that this hydrate may very easily be obtained. Sulphuric acid, which had been rectified over sulphate of potash, deposited at 28°·4 F. some large right-rhombic prisms more than an inch in thickness. One of these crystals melted at 71°·6 in the air in the course of twenty minutes; the liquid acid obtained had the specific gravity 1·784 at 46°, which agrees very well with the number usually adopted, 1·708.

The production of large and regular crystals depends chiefly upon the degree of concentration of the acid. The acid just mentioned, procured by melting a crystal of 1·784 spec. grav., solidified entirely at 24° ; whilst a more concentrated acid of 1·7885 spec. grav., at 24° left a liquid residue of the hydrate SO^3 HO when cooled to 21°. The crystals are most easily obtained from acids of precisely this degree of concentration : Berzelius has stated that crystals are most easily procured by the addition of somewhat less than 1 atom of water to SO^3, HO. If the sulphuric acid contains more than 2 atoms of water, the crystalline hydrate only separates at a very low temperature.—*Archiv der Pharm.*, lviii. p. 23.

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On the Estimation of Nitrous Acid. By H. Schwarz.

In analysing some nitrites, I have, in determining the NO^3, turned to account its property of being instantly decomposed by urea into

* Chem. Gaz., vol. vi. p. 345.

CO^2N*. $C^2N^2H^4O^2+2NO^3=2(CO^2)+4N+4HO$. For this purpose the salt is conveyed into one of the little flasks of the apparatus described by Will and Fresenius, a solution of urea added, the stopper fixed in its place, weighed, and the sulphuric acid drawn over. The operation is soon finished; and when sufficient air has been drawn through, the amount of CO^2 and N which has escaped is found very accurately by weighing. A loss in weight of 1·000 corresponds to 0·7600 nitrous acid. I found in a double salt of nitrite of lead and potash given me by Prof. Fisher, 28·91 and 29·33 per cent. of nitrous acid. On determining the oxide of lead and potash, 29·20 per cent., was found by the loss for the nitrous acid. Liebig's *Annalen*, April 1849.

On a Phosphatometric Process for the purpose of ascertaining the Quality of Manures, and more particularly the black Residuum of Refineries. By MM. Ed. Moride *and* Ad. Robierre.

In the course of the experiments which we made upon the residuum of refineries, we employed, in order to ascertain the quantity of phosphate of lime in animal charcoal, a process to which we think proper to call the attention of agriculturists and persons desirous of analysing manures.

Combined with the simple means given by M. Peligot for ascertaining the quantity of nitrogen contained in any substance†, the *phosphatometric* method which we employ allows of the principal elements of manures being readily discovered. We will now briefly describe this method, taking for example the analysis of the black residuum of a refinery:—

It is to be dried at a temperature of 212° F., and a certain quantity (say 1 grm.) weighed off and incinerated in a platinum crucible. To the red ash a small quantity of carbonate of ammonia is to be added, in order to carbonate the lime which has been rendered caustic by the calcination, and the residuum is weighed. The difference in weight indicates the carbon and the organic matter. The ash obtained is thrown upon a filter, and washed with boiling water; the soluble salts are thus removed by the water.

When the water of filtration no longer yields a precipitate in the presence of chloride of barium, the filter, with the washed ash which it contains, are calcined in a platinum crucible; the residuum is then weighed, deducting the weight of the filtered ash, which should be previously ascertained. The difference in weight of the ash, before and after washing, gives the quantity of soluble salts in the water. This quantity rarely exceeds from 1 to 2 per cent. of the residuum.

The ash is introduced into a closed tube, and dissolved at a low heat in the smallest possible quantity of pure nitric acid. When the solution is completed, the whole is poured into a glass vessel,

* The same reaction has been made use of by M. Millon for the estimation of urea.

† Chem. Gaz., vol. v. p. 183.

care being taken to carefully remove the slightest traces of liquid which may be contained in the closed tube.

The liquid thus obtained contains phosphate and (carbonate of) lime, alumina, oxide of iron and magnesia; it also holds in suspension silica, which might be estimated by simple filtration, but which is not taken any notice of when the object is only to ascertain the quantity of phosphate contained in the substance submitted to analysis. The liquid is now very carefully saturated with pure ammonia, which is poured in drop by drop, stirring at the same time with a glass rod. Each drop of ammonia, as it falls into the solution, produces a precipitate of phosphate of lime, which is rapidly dissolved by agitation; but after a certain time it becomes insoluble; no more ammonia must then be supplied. It is very important that the precipitate should cause but slight cloudiness, and with a little practice the moment of transition may be readily ascertained; the liquid is at that time slightly acid. A few drops of acetic acid are added, in order to redissolve as quickly as possible the phosphate held in suspension.

We have remarked that the liquid generally remains turbid, especially if the nitric solution of the phosphate of lime is prepared at too great a heat. The operator should therefore pay great attention to this point.

The process which has been found the most simple, and at the same time the most correct and expeditious, for arriving at the quantity of phosphate of lime, consists in the employment of a normal solution of acetate of lead, which is poured into the dissolved phosphate until iodide of potassium indicates an excess of oxide of lead in the mixture, which has been carefully alcoholized.

For the composition of our normal liquor, we took for basis the composition of the phosphate of lead, obtained as above described. We ascertained that this phosphate was a mixture of sesquiphosphate and a small quantity of biphosphate of lead. Its composition was as follows:—

Phosphoric acid.....	20 parts.
Oxide of lead.....	80 ...
	100

We have therefore based our calculations upon quantities which experience has shown to be constant, and we have estimated the quantity of pure acetate of lead necessary for representing 80 of oxide of lead. This quantity is equal to 136·26. Now 100 parts of phosphate of lead obtained by us represent by their phosphoric acid 43·85 of phosphate of lime from bones, adopting for this latter body the formula $PhO^5, 3CaO$, admitted by M. Raewsky; consequently 310·74 will represent the quantity of pure crystallized acetate of lead necessary for saturating the acid in 100 parts of phosphate of lime, or 3·107 grms. for one gramme; the 3·107 grms. dissolved in the water will constitute 50 cubic centimetres of normal liquid. A litre (about a quart) of liquid ought therefore to contain 62·14 grms. of acetate of lead. Care must be taken to acidify this liquid with a little acetic acid.

50 cubic centimetres of normal liquid, introduced into an alkalimetric vessel, will saturate 1 grm. of phosphate of lime from bones; that is to say, the vessel being graduated into 100 parts, each degree will represent 1 centigramme of phosphate.

The operator having filled the graduated vessel, takes a thin plate of glass, on the surface of which he deposits with a glass rod 10 drops of iodide of potassium. He then pours the normal solution of lead into the solution of phosphate, saturated with ammonia as above stated, stirring it briskly after each fresh addition; phosphate of lead is immediately produced, and precipitated with remarkable rapidity.

If at this moment the end of a glass rod be moistened at the surface of the mixture, so as not to touch the phosphate which is deposited, but merely the supernatant liquor, and if the drop thus obtained be brought into contact with one of the iodized drops deposited upon the glass plate, the reaction produced will easily show whether there is or is not an excess of oxide of lead in the liquor. It will, in fact, be understood that as long as there is any phosphate to decompose, the oxide of lead of the acetate will be converted into phosphate of lead.

At a certain moment (and this is a fact both curious and useful) the iodide of potassium causes the liquid to assume a yellow colour, at a time too when it might be supposed that the proper proportions had been used; but this is not the case. At this moment, the phosphate being almost entirely decomposed, the acid in excess in the liquor exercises a feeble reaction upon the phosphate of lead, and determines its solubility. This tendency to dissolve is however very weak, but sufficient to communicate to iodide of potassium a yellow colour, which serves as a test.

This test gives a tolerably correct notion of the richness of the substance in phosphate of lime; for, as we shall presently see, this previous yellow colouring produced upon the plate of glass takes place very little before the completion of the operation.

To the liquid two-thirds of its volume of alcohol are added, in order to neutralize the slight degree of solvent power possessed by the excess of acid; and from this moment the plumbic solution is to be carefully poured in, care being taken to stir with a glass rod, and to allow of phosphate of lead depositing, before touching the surface of the mixture with the rod. As soon as the drop acquires a greenish-yellow colour by contact with the iodide of potassium, the operation must be stopped; the amount of phosphate contained in the manure may then be ascertained by observing the degree marked on the graduated glass.

When the acetate of lead employed is not perfectly pure, it will be necessary to make a previous experiment by dissolving a known quantity of phosphate of lime; and the result of all subsequent experiments may be ascertained by a simple calculation of proportion.

This phosphatometric operation requires but a few minutes for its execution, and furnishes results the correctness of which it is very difficult otherwise to arrive at when phosphates mixed with

alumina are to be operated upon. It may be briefly described as consisting of the following operations:—

1. Solution in nitric acid of the matter deprived of its soluble salts by water.

2. Saturation with ammonia until the appearance of a slight precipitate, which is redissolved in a few drops of acetic acid.

3. Saturation of the phosphoric acid by means of the normal solution of acetate of lead.

4. Addition of a quantity of alcohol equal to two-thirds of the whole volume, as soon as a drop obtained from the surface of the liquid causes iodide of potassium (placed upon glass) to assume a yellow colour.

5. Observation of the moment when an excess of lead salt appears in the liquid mixed with alcohol.

If, as stated by M. Dumas, there is any utility in ascertaining the quantity of phosphates in manures, we think we have much simplified the means of arriving at a desirable result.—*Technologiste*; and Newton's *Journal*, May 1849.

On the Estimation of Starch. By H. Schwarz.

Krocker's experiments have shown that it is not impossible to convert starch entirely into grape-sugar; he then determines the amount of sugar produced in Will's apparatus from the quantity of carbonic acid which is evolved during the fermentation. I believe that Barreswil's method of estimating the grape-sugar by means of a solution of copper deserves the preference as regards the time necessary for its execution. For this purpose, a strong alkaline solution of oxide of copper is prepared with the aid of tartaric acid, which prevents the precipitation of the oxide of copper. The best proportions are—

50 grms. $KO+HO+\overline{T}$
20 grms. $NaO+CO^2$
40 grms. $KO+HO$ dissolved in 200 cubic centim. water.

On the other hand, 30 grms. of $CuO+SO^3+5aq$ are dissolved in 100 cubic centim. water. The two liquids mixed furnish a dark blue liquid, which is filtered and diluted so as to form half a litre.

Supposing us to have pure starch, 10 grms. of it are weighed off after it has been well dried, and converted by boiling with dilute sulphuric acid into grape-sugar, the liquid is likewise transferred into the half-litre measure, and diluted so as to form 500 cub. centim. Instead of the pure starch, the equivalent amount of cane-sugar (white sugar-candy) can be weighed off and converted into grape-sugar.

10 grms. of starch correspond to 10·555 grms. grape-sugar.

So much of this normal solution of starch is added to 50 cub. centim. of the solution of copper, constantly boiling, until it is entirely decolorized, with formation of protoxide of copper, and the quantity used is noted down. Suppose it, for instance, to require 50 cub. centim., then it corresponds to 1 part of pure starch.

Now if 10 grms. of flour are treated exactly in the same way, and the solution of starch-sugar produced likewise diluted so as to form half a litre, and then attempt be made to reduce the same 50 cub. centim. solution of copper, I shall now require a much larger quantity, for instance 75 cub. centim. These 75 cub. centim. correspond therefore to 1 grm. of pure starch; the 500 cub. centim. consequently to 6·666 grms.; the 10 grms. of flour contain consequently 6·666 grms. of $C^{12} H^{10} O^{10}$, or 66·66 per cent. of starch.—Liebig's *Annalen*, April 1849.

CHEMICAL PREPARATIONS.

On the Preparation of Succinic Acid from Malate of Lime. By Prof. Liebig.

The highly important and beautiful observations of Dessaignes on this subject* induced me to examine whether the malate of lime might not be converted more rapidly and perfectly into succinate of lime by an ordinary process of fermentation than by the plan proposed by that chemist, and whether an advantageous method of manufacturing succinic acid on a large scale might not be founded upon it.

These experiments have been crowned with complete success. The decomposition of the malate of lime can be effected far more easily and rapidly than the conversion of the lactate of lime into butyrate, by employing the same ferment as is used in the butyric acid fermentation. The malic acid is decomposed under these circumstances into succinic, acetic and carbonic acids.

When to a mixture of 1 part malate of lime and 5 to 6 parts of water the tenth part of the volume of the water of ordinary yeast is added, a pretty lively evolution of gas soon ensues when the mixture is placed in a warm situation. The gas which is disengaged is pure carbonic acid, and is absorbed without the least residue by potash.

After three days an essential change in the form of the malate of lime is perceptible; it becomes granular, heavy and crystalline, and in the course of the fermentation these granules increase constantly in size. When the fermentation is complete, *i. e.* when the evolution of gas has ceased, the mixture loses on agitation its muddy condition; the granules appear under the microscope to be composed of stellate groups of transparent needles, which quickly subside like heavy sand when stirred. These crystals consist of a double salt of succinate of lime with carbonate of lime. The supernatant liquid contains acetate of lime.

The formation of succinic acid is effected with equal ease and rapidity by putrefying fibrine or putrefying cheese; the latter is especially adapted for this purpose; the following proportions prove to be

* See Chem. Gaz., p. 69 of the present volume.

most advantageous:—3 lbs. of crude malate of lime, as it is obtained from the expressed juice of the berries of the mountain ash*, after being twice or thrice washed with water, is mixed with 10 lbs. of water at 104° F. in an earthen pan, and 4 oz. of putrid cheese, which has been previously rubbed into an emulsion with water, is added to the mixture. When kept between 86° and 104°, a disengagement of gas very soon begins, which continues from five to six days (longer at a lower temperature). In another experiment with 15 lbs. of malate of lime, the fermentation was over in four days.

When every sign of fermentation has disappeared, the granular crystalline deposit is collected upon a strainer, washed several times with cold water, and the succinic acid then separated by means of sulphuric acid. For this purpose the crude succinate (and carbonate) of lime is mixed with dilute sulphuric acid until no further effervescence is perceptible, and the quantity of sulphuric acid consumed is noted down. Upon this an amount of dilute sulphuric acid equal to that consumed is added to the paste, and the entire mixture heated to boiling, and kept at this temperature until the granular consistence has entirely disappeared. The liquid is separated from the gypsum formed by filtration through a linen bag, the gypsum washed, and the acid liquid concentrated by evaporation; it contains in solution a mixture of bisuccinate of lime with succinic acid. When it has been so far evaporated that a crystalline pellicle begins to form on the surface, concentrated sulphuric acid is added to it in small portions until no further precipitate of gypsum is formed. In general the liquid congeals to a pasty mass by the newly formed gypsum; it is diluted with water, and the succinic acid separated by washing. On evaporating the liquid and cooling, a crop of brownish-coloured crystals of succinic acid separates, which contains minute traces of gypsum. This coloured acid is dissolved in boiling water, filtered, set aside to cool, the crystals thrown upon a funnel, and the mother-liquor removed with cold water. The acid obtained by this second crystallization is again dissolved in water, boiled with a little animal charcoal, and the transparent solution crystallized. The crystals are of a dazzling white; they can easily be freed from a trace of gypsum by solution in alcohol or sublimation. 3 lbs. of dry malate of lime furnished from 15 to 16 oz. of dazzling white succinic acid. In my experiments not a trace of malic acid was found in the mother-liquor from the succinic acid; so that in this remarkable process of fermentation the whole of the malic acid is completely decomposed. The process with putrid cheese differs from that with yeast in hydrogen gas being disengaged along with the carbonic acid towards the end of the operation.

Science is indebted to M. Dessaignes for this beautiful discovery, and it is to be hoped that fermentation will come more into use as one of the most powerful agents for chemical decompositions. It is

* In this country the malate of lime might probably be obtained from culinary rhubarb according to the process described by Mr. Everitt, Chem. Gaz., vol. i. p. 248.

easy to prepare from malate of lime any amount of this interesting but hitherto expensive acid; and a number of useful applications may possibly follow from this discovery.—Liebig's *Annalen*, April 1849.

On the Preparation of Hydrobromic and Hydriodic Acids. *By* C. H. Mène.

Hitherto hydrobromic and hydriodic acids have been prepared by decomposing the phosphurets of bromine and iodine by a small quantity of water. Now without mentioning the considerable loss of substance, the serious and frequent accidents which occur in this reaction frequently prevent chemists from preparing these gases, and consequently of studying their properties. The means recently proposed, as the essential oil of lemon, or naphthaline, being either rare, expensive or of difficult preparation, I have considered it of sufficient importance to describe a new method of preparation, which I have recently employed with success, and which presents no danger and is not accompanied by any loss.

To liberate hydrobromic acid gas, I employ the crystallized hypophosphite of lime obtained in the preparation of phosphuretted hydrogen from phosphuret of calcium. It is placed in a flask or retort with a small quantity of water; after which I add, by means of a long funnel, some liquid bromine; the reaction takes place instantly, without the assistance of heat, and hydrobromic acid is disengaged, and may be collected over mercury. It is merely requisite to place in the neck of the retort or the flask some pieces of cotton or of amianthus, in order to retain any bromine vapour which might be volatilized by the heat. The reaction of the bromine upon the hypophosphite of lime in presence of water will be easily understood; the water is decomposed, 4 parts of oxygen pass to the hypophosphite of lime, converting it into neutral phosphate, and the 4 parts of hydrogen are transferred to the bromine, forming hydrobromic acid:—

$$4Br + PhO, CaO + 4HO = PhO^5\,CaO + 4HBr.$$

To prepare hydriodic acid, I use the same salt and follow the same mode of preparation, only it is requisite to assist the reaction by a little heat. The decomposition is similarly expressed by the equation

$$4I + PhO, CaO + 4HO = PhO^5 + 4HI.$$

Sulphite of soda may likewise be employed for the preparation of these two gases. With this salt it is not necessary to add water, as in general the crystals of commerce contain a sufficient quantity; I merely dip them in water, and then add immediately the bromine or iodine. It is necessary to assist the reaction by heat. The reaction is very simple. The bromine or iodine decomposes the water in presence of this salt; 1 equiv. of hydrogen is transferred to the bromine, forming the gas in question, and the oxygen converts the sulphite into sulphate:—

$$SO^2, NaO + HO + Br \text{ or } I = SO^5\,NaO + BrH \text{ or } IH.$$

It needs scarcely to be observed that the last method is preferable, as the sulphite of soda is commonly met with in commerce, whilst the preparation of the hypophosphite of lime is very troublesome. In the course of two weeks I have disengaged from 20 to 25 litres of these two gases without having met with the least accident; whilst with the old process I have frequently had explosions, which would certainly have produced serious consequences if the quantities operated upon had been at all considerable.

The proportions to be employed for the preparation of these two acids are—

By the hypophosphite of lime.		By the sulphite of soda.	
Water	1	Water	1
Iodine or bromine	5	Iodine or bromine	3
Hypophosphite in crystals	4	Crystallized sulphite of soda	6
For 10 parts.		For 10 parts.	

Comptes Rendus, April 9, 1849.

PATENT.

Patent granted to Alexander McDougal *and* Henry Rawson *for Improvements in the Manufacture of Sulphuric Acid, Nitric Acid, Oxalic Acid, Chlorine and Sulphur.*

The first part of this invention relates to the manufacture of oxalic and nitric acids. It consists,—1st, in the substitution of rice for sugar or starch in the manufacture of oxalic acid; and 2nd, in a method of treating the nitrous gases or fumes which are given off from the action of nitric acid upon the sugar, starch, rice, or other organic substances used in making oxalic acid.

The following is the method of treating the nitrous fumes:—The fumes are conveyed into a vessel containing water by a pipe dipping below the surface of the water; air is permitted to enter into the vessel and mix with the gas, which bubbles up through the water; and the mixture of gas and air is drawn by a pneumatic apparatus through a series of vessels similar to the first, each having a tube dipping into the liquid, and being connected by a tube at the top with the next vessel. The nitrous gas is thus made to pass alternately into air and water, and is by this means converted into nitric acid. The patentees state that the reaction which ensues may be best expressed by the use of chemical symbols as follows:—When $3NO^4$ is passed into water at a temperature of 100° F., or upwards, $2NO^5 + NO^2$ results; the $2NO^5$ (*i. e.* 2 atoms of nitric acid) remain in solution, while the NO^2, which is an uncondensable gas, bubbles through the liquid, and, mixing with the air in the vessel above the liquid, takes 2 atoms of oxygen from the air and becomes NO^4; which, passing again through the liquid, becomes nitric

acid and nitrous gas as before; and thus nearly the whole of the nitrous fumes or gas is reconverted into nitric acid. The nitric acid thus obtained may be used again for making oxalic acid, or for any other purpose to which nitric acid can be applied. There are several chemical processes in which nitrous gas is given off, and to each of these the above method of treating the gas or fumes may be applied.

The second part of this invention consists in a method of manufacturing sulphuric acid, by the use of a series of vessels similarly arranged to those above mentioned, only that the first vessel is connected with a sulphur-burner. The first vessel is charged one-third full of nitric acid, and the others one-third full of water; the burner is then charged with sulphur; and lastly, the pneumatic apparatus connected with the last vessel is put in action. Air being thus drawn over the ignited sulphur, sulphurous acid and air pass into the nitric acid in the first vessel, where a portion of the sulphurous acid is converted into sulphuric acid at the expense of the nitric acid; the uncondensed sulphurous acid passes with the air and nitrous gas into the second vessel; and so they pass alternately into water and air until the processes of oxidation and condensation are completed. When the working has been continued for some time, it will be found that the nitric acid has entirely left the first vessel, which now contains sulphuric acid nearly pure. The same would take place with each of the other vessels, if the nitric acid, which has been condensed in the vessels toward the end of the series, was not returned to the first vessel; so that when the first vessel is exhausted of nitric acid, the sulphuric acid which it contains must be removed, and the vessel supplied with nitric acid from the vessels lower in the series. Sulphuric acid is thus obtained without the loss of any nitric acid, as the lower oxides of nitrogen given off in the oxidation of sulphurous acid are again converted into the higher oxides, and again used for the conversion of sulphurous into sulphuric acid.

The third part of this invention consists in the following improvements in the manufacture of chlorine:—Any of the chromates or bichromates are treated with hydrochloric acid, either in its free or nascent state; and thereby chlorine is given off, and a chloride or sesquichloride of chromium and a chloride of the base of the chrome salt are formed. The latter products are treated with nitric acid, and the hydrochloric acid distilled off; and thereby nitrates of chrome and of the base of the original chrome salt are obtained. The nitrates being exposed to heat, the lower oxides of nitrogen are given off; and these are oxidized and condensed, as described in the first part of the invention. By the action of heat upon the nitrates, the patentees also obtain, after the oxides of nitrogen have been driven off, the chromate or bichromate first employed, which may be used in the production of chlorine as before. The chromate of lime is preferred to be employed in the above process.

The fourth part of this invention consists in manufacturing sulphur by passing sulphuretted hydrogen through a heated tube. By this means the gas is decomposed, sulphur being deposited and hydrogen given off.—Sealed Nov. 21, 1848.

THE CHEMICAL GAZETTE.

No. CLXIII.—August 1, 1849.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On a Series of insoluble Alkaline Salts of Phosphoric and Arsenic Acids. By H. Rose.

Of the double salts of the earthy and alkaline phosphates insoluble in water, the ammonio-phosphate of magnesia was the only one hitherto known; but perfectly analogous double salts of potash and soda, as also of lithia, both with magnesia and lime, can be produced. These double salts are formed on fusing phosphate of lime or magnesia with an excess of carbonated alkali; but they cannot be obtained pure in this way, as a partial decomposition always takes place from the great excess of the alkaline carbonate. The higher the temperature at which the decomposition occurs, and the more perfect the whole becomes liquid, the greater is the amount of earthy phosphate decomposed. In fact, perfect decomposition may result under certain conditions with the phosphate of magnesia; but this never obtains with the phosphate of lime, and the reason of this is, that the double salt of alkaline phosphate and phosphate of lime is decomposed with great difficulty by the alkaline carbonate.

When, however, the earthy phosphates are well mixed with a small quantity of carbonated alkali, and then heated so that the mass neither melts nor can cake together, the whole of the carbonic acid is expelled from the alkali, and the latter cannot be completely removed from the calcined compound either by cold or by hot water. It is however difficult to obtain these compounds in a state of great purity, which depends partly on the quantity of carbonated alkali employed; if too little is used, a compound is obtained mixed with excess of earthy phosphate; whilst if too much is employed, a slight decomposition may occur, and the compound then contains more or less earthy carbonate. But the composition of the compound likewise depends partly on the length of the washing, by which they are more or less altered.

In general 1 atom of the earthy pyrophosphate was mixed intimately with 1 atom of the alkaline carbonate, and the mixture calcined until no further loss in weight resulted. The calcined mass had not fused nor caked together; it was heated for some time with water, and then washed with hot water.

On analysis the compounds were found to consist more or less accurately of 2 atoms of earth, 1 atom of alkali and 1 atom of phos-

phoric acid; and the oxygen of the bases was to that of the phosphoric acid as 3 : 5.

In most cases the washing required considerable time; in some cases it was almost impossible to accomplish it. It was then found that the alkali was very tenaciously retained, but that a large, frequently the largest portion, had been removed from the earthy phosphate by the washing. In these cases the alkali is replaced by an equivalent of water; so that such a compound, after having been washed a long time with hot water, consists partially of the still undecomposed original compound, but partially of a new one consisting of 2 atoms of earth, 1 atom of water and 1 atom of phosphoric acid, both compounds mixed or combined with each other. When, in the preparation, an excess of carbonated alkali has been used and the earthy phosphate fused with it, the washed compound is mixed with larger or smaller quantities of earthy carbonate. The water which has been used for the washing never presents the least trace of carbonic acid unless an excess of alkaline carbonate has been employed, but always larger or smaller traces of alkali. But sometimes some of the earthy phosphate is dissolved by the washing, and the presence of phosphoric acid and of the earth can be detected in the wash-water by reagents. In this case the compound was washed with water to which a little ammonia had been added.

Nearly all the salts examined exhibited a crystalline structure under the microscope. For analysis the compounds were dried at 212°, and a portion then calcined; in many cases this occasioned a slight loss in weight, which arose from water, as the other portion of the dried salt, treated with nitric acid in a suitable apparatus for determining carbonic acid, gave off in most cases none or the merest trace of carbonic acid. Only in a few cases did carbonic acid (as earthy carbonate) form an essential constituent, or rather admixture, of the compound; but in such cases, as above observed, more alkaline carbonate had been employed to produce the salt than requisite. In such cases the wash-water contained larger quantities of phosphoric acid, and the amount of alkali in the insoluble compound was smaller in proportion.

In order to separate the bases from the phosphoric acid, the solution of the salts in nitric acid was treated with metallic mercury. The earths were separated from the alkalies according to the usual methods.

Phosphate of Potash and Lime, $KO+2CaO+PO^5$.—The compound, dried at 212°, experienced no loss at a gentle red heat. After estimating the carbonic acid by means of nitric acid in a small apparatus, the bases were separated by mercury as above described. The following results were obtained:—

		Oxygen.		Calculated according to the formula.
Lime	32·71	9·18	13·51	32·10
Potash	25·59	4·33		26·96
Phosphoric acid	39·73	22·26		40·84
Carbonic acid	0·66			

A slight decomposition had been occasioned by a very small excess of carbonate of potash, and some carbonate of lime formed. In other respects the calculated composition agrees very well with that found.

Phosphate of Soda and Lime, $NaO+2CaO+PO^5$.—In one experiment, to prepare the salt, the quantity of carbonate of soda used was much greater than required; the calcined mass had become caked together, and the wash-water contained a considerable amount of phosphoric acid. In a second experiment (II.) the requisite quantity of carbonate of soda was employed:—

	I.	Oxygen.		II.	Oxygen.	
Lime	40·17	11·23	12·60	35·27	8·56	14·34
Soda	5·17	1·32		19·12	5·76	
Phosphoric acid	41·39	23·19		44·90	26·28	
Carbonic acid	13·49					

A third experiment was made to ascertain whether, on fusing phosphate of lime with a large excess of carbonate of soda, the resulting compound, washed with water, would contain alkali. This salt, dried at 212°, gave—

	III.	Oxygen.
Lime	47·60	13·37
Soda	5·25	1·34
Phosphoric acid	33·15	18·57
Carbonic acid	9·11	6·59
Water	4·89	4·34

The water was determined from the loss, as it could not be found by ignition, owing to the presence of carbonate of lime; the compound contained a considerable quantity of carbonate of lime mixed with it, and besides the compound $NaO+2CaO+PO^5$, nearly 3 atoms of $HO+2CaO+PO^5$. The analysis shows an excess of water; it is however found by the loss, and is consequently made up of all the small losses of the other constituents.

Phosphate of Potash and Strontia, $2SrO+KO+PO^5$.—The compound, dried at 212°, experienced no perceptible loss on ignition. It afforded—

		Oxygen.	Calculated according to the above formula.
Strontia	49·33	7·62	46·59
Potash	17·62	2·98	21·24
Phosphoric acid	34·01	19·08	32·17

Some potash has been removed from the compound by the washing.

Phosphate of Soda and Strontia.—

		Oxygen.
Strontia	53·44	8·25
Soda	10·16	2·59
Phosphoric acid	34·61	19·39
Water	1·72	1·53

The per-centage composition of a compound represented by the formula $NaO+2SrO+PO^5$ would be,—strontia, 50·19; soda, 15·15;

and phosphoric acid, 34·66. The compound examined corresponds very closely to the formula $2(NaO+2SrO+PO^5)+(HO+2SrO+PO^5)$, which would require—

Strontia	52·07
Soda.....	10·47
Phosphoric acid	35·95
Water	1·51

Phosphate of Potash and Baryta.—This compound appears to be more decomposed by treatment with water than all those hitherto described. It furnished on analysis—

		Oxygen.
Baryta.....	70·23	7·34
Potash.....	1·55	0·26
Phosphoric acid	26·95	15·10
Water	2·36	2·09

It appears as if the phosphate of baryta, which was employed as $2BaO+PO^5$, had only been deprived of phosphoric acid by ignition with carbonate of potash, and had become converted into $3BaO,PO^5$. The compound moreover contains some $KO+2BaO+PO^5$ and $HO+2BaO+PO^5$.

Phosphate of Soda and Baryta.—The compound, dried at 212°, gave—

		Oxygen.	Calculated according to $NaO,2BaO+PO^5$.
Baryta	65·45	6·83	59·85
Soda	7·10	2·04	12·28
Phosphoric acid..	26·54	14·86	27·87
Water	1·07	0·95	

It had therefore been somewhat decomposed by water, and contained, besides $NaO+2BaO+PO^5$, some $HO+2BaO+PO^5$.

Phosphate of Potash and Magnesia.—Only slight traces of phosphate of magnesia dissolved on washing the salt which had been calcined with carbonate of potash. The compound, dried at 212°, had the following composition :—

		Oxygen.	Calculated according to $KO,2MgO+PO^5$.
Magnesia	28·45	11·01	25·85
Potash	22·15	3·75	29·48
Phosphoric acid..	46·88	26·26	44·67
Water	2·52	2·23	

In this case some potash has been removed by washing and replaced by water.

Phosphate of Soda and Magnesia :—

		Oxygen.
Magnesia	34·82	13·47
Soda	11·75	3·00
Phosphoric acid.....	45·00	25·21
Water.....	8·13	7·20

This compound contains $NaO+2MgO+PO^5$ and $3MgO+PO^5$. It is difficult to account for the large amount of water.

Phosphate of Lithia and Lime.—For these experiments pure carbonate of lithia was employed perfectly free from potash and soda. As is well known, the carbonate of lithia is essentially distinguished from the carbonate of potash and soda by a very peculiar property. When fused in a platinum crucible, it acts upon it, and the platinum acquires a liver-brown coating where the readily fusible salt was in contact with it. On the discovery of lithia, great importance was attached to this property, and it was considered to furnish a distinctive character between lithia and the other fixed alkalies. Only the carbonate of lithia has this property, and none of the other readily fusible salts of lithia. In those compounds, for instance, the silicates, in which the presence of lithia was suspected, it was customary to fuse them before the blowpipe with carbonate of soda upon platinum foil; subsequently however it was found that the coating of the platinum in this case was a very uncertain test for lithia, since pure carbonate of soda fused upon platinum foil frequently produced a similar appearance. The brown coating of the platinum disappears when the spot is washed with water and heated to redness, but the metal has lost its polish and become deadened.

This colouring of the platinum on fusion with carbonate of lithia arises from its losing some carbonic acid at a red heat; the lithia, the moment it is liberated, causes the platinum to oxidize, and combines with the oxide in a similar manner, as is the case with potash and soda when they are set free, or when they act as hydrates at a high temperature upon platinum. The ready fusibility of the carbonate of lithia favours the oxidation of the platinum far more than when the carbonates of the alkaline earths are heated in a platinum crucible to intense redness.

The loss in carbonic acid which the carbonate of lithia experiences is not very considerable; 0·603 grm., after being fused six times, only decreased 0·023 grm. 1 atom of carbonate of lithia was heated with 1 atom of phosphate of lime ($2CaO, PO^5$); the whole of the carbonic acid was expelled. The compound, dried at 212°, furnished—

		Oxygen.	$LiO,2CaO+PO^5$ requires
Lime	41·53	11·76	39·58
Lithia.....	9·03	4·98	10·22
Phosphoric acid....	50·69	28·39	50·20

When the earthy phosphates are fused with alkaline chlorides, chlorine is expelled on the access of moist air as hydrochloric acid, and compounds similar to those above described are formed.

When however earthy phosphates are contained with alkalies in acid solutions, the former can be precipitated by ammonia without the precipitate containing alkali. These compounds therefore are not formed in the humid way; the whole amount of the earthy phosphate however is not precipitated.

Besides the phosphates above described, others appear to be

formed under certain circumstances, which perhaps consist of 2 atoms of an alkali, 1 atom of an earth and 1 atom of phosphoric acid. They are soluble in water. When an organic substance is carbonized and the charred mass is exhausted with water, the aqueous solution very frequently contains earthy phosphates (especially phosphate of lime), which separate when the liquid is evaporated to dryness and the residue is dissolved in water. The earthy phosphates are held in solution by the alkaline phosphates, with which they have formed soluble double salts.

When an excess of pyrophosphate of soda is heated to a faint red with carbonate of lime, the aqueous solution of the ignited mass contains phosphate of lime. The presence of lime can instantly be detected by oxalic acid in the aqueous extract. The phosphate of lime does not separate well when the aqueous extract is evaporated to dryness, or when a current of carbonic acid gas is passed through it; but it is entirely deposited when carbonate of soda is added to the liquid and then evaporated. The separated phosphate of lime contains no carbonate of lime after washing. Evidently a soluble double salt of phosphate of soda and phosphate of lime is formed; the latter separates when a portion of soda in the solution is converted into carbonate.

Arseniate of Potash and Magnesia.—Dried ammonio-arseniate of magnesia was kept at a gentle heat until the whole of the water and ammonia might be assumed to be expelled; it was then intimately mixed with 1 atom of carbonate of potash, and heated to redness in a porcelain crucible. The calcined mass, which had not caked together, was boiled with water and well washed; the washing was effected with water containing some ammonia. The filtered liquid contained a large amount of arsenic acid; the residue, which had been washed for a very long time, gave a copious evolution of carbonic acid on treatment with hydrochloric acid; however, the solution, upon being supersaturated with ammonia, furnished a large precipitate of arseniate of ammonia and magnesia; another portion of the solution, mixed with alcohol and chloride of platinum, produced but a very slight precipitate of the potassio-chloride of platinum. The earthy arseniates are far more perfectly decomposed than the phosphates by fusion with alkaline carbonates. The decomposition would have been complete had a larger amount of carbonate of potash been used; for even a small amount decomposed a very considerable quantity of the arseniate of magnesia; nevertheless a compound, $KO+2MgO+AsO^5$, had been produced, which was decomposed by the water.

Arseniate of Soda and Magnesia.—This compound was boiled with water, and washed with water containing a little ammonia. The filtered liquid contained no carbonic acid, but a large amount of arsenic acid. The compound did not exhibit a trace of carbonic acid on treatment with nitric acid. The bases were separated with metallic mercury. To estimate the arsenic acid, another portion of the compound was dissolved in muriatic acid, and the solution supersaturated with chloride of ammonium and ammonia. From the

precipitate of ammonio-arseniate of magnesia the amount of arsenic acid was calculated; the filtered liquid contained not a trace of arsenic acid. The arseniate of magnesia can therefore be entirely precipitated by ammonia, which is not the case with the (pyro)phosphate of magnesia. Analysis gave—

		Oxygen.	$NaO, 2MgO + AsO^5$ requires
Magnesia	24·28	9·40	22·02
Soda	11·50	2·94	16·62
Arsenic acid	57·52	19·97	61·36
Water	6·70		

The water is determined from the loss. It is seen from this examination, that on heating arseniate of magnesia and carbonate of soda, a portion of the former is decomposed; arseniate of soda and carbonate of magnesia are formed, which however on calcination is wholly deprived of its carbonic acid. The mass treated with water evidently contained the compound $NaO + 2MgO + AsO^5$; which however was partly converted, by treatment with water, into $HO + 2MgO + AsO^5$, and pure magnesia produced from the carbonate. —Poggendorff's *Annalen*, June 14, 1849.

Chemical Facts applied to Physiology. By M. Barreswil.

The following are the conclusions arrived at by the author:—

1. That the white of the egg of the common fowl contains sugar.
2. That the white of egg is alkaline, and that its alkalinity depends upon carbonate of soda.
3. The yolk of egg contains little or no alkali; its emulsive properties in all cases depend, not upon the alkali, but upon a product analogous to that existing in the pancreatic juice.
4. The yolk of egg is not acid, but becomes so in consequence of having undergone a change.
5. The acid reaction and the properties of the gastric juice are produced by organic acids, and not muriatic acid.
6. The alkali and sugar of the white of egg may disappear, mutually destroying each other, even during the experiment made for their demonstration; and thus the discrepancy in the results obtained by the difference of the methods may be explained.
7. The change in the albumen of the egg, and in all analogous matters, is more rapid in proportion to the dilution of these matters; and the cause of the greater or less rapidity in the change is owing (all other conditions being the same) to the circumstances which favour more or less the solution of the ferment.—*Comptes Rendus*, June 18, 1849.

Action of Water on Leaden Service-Pipes. By E. N. Horsford, *Professor of Chemistry in the University of Cambridge, U.S.*

The following extracts are taken from a very important investigation published in the Proceedings of the American Academy of

Arts and Sciences, for a copy of which we are indebted to the kindness of the author. The researches were undertaken at the request of the Board of Consulting Physicians of the city of Boston, and extend to fifty pages of closely-printed letter-press. We give the author's conclusions, which have more than a local interest, and the method which he proposes for determining small quantities of lead, which promises to be of considerable service in such investigations :—

The waters used by man in the various forms of beverage and for culinary purposes are of two classes, viz.

1. *Open waters, derived from rain-falls and surface-drainage, like ponds, lakes, rivers and some springs*; *and*

2. *Waters concealed from sunlight, and supplied by lixiviation through soils or rock, or both, of greater or less depth, such as wells and certain springs**.

They differ, (*a.*) in temperature; well water, through a large part of the year, is colder than lake, pond or river water; (*b.*) in the per-centage of gases in solution; recently drawn well water, in summer particularly, parts with a quantity of air upon exposure to the surface temperature. In winter these relationships must to some extent be inverted, in high latitudes for a longer, and in lower latitudes for a shorter period.

(*c.*) They differ in the per-centage of inorganic matter in solution; well waters contain more; (*d.*) in the relative proportions of salts in solution; well waters contain more nitrates and chlorides; and (*e.*) in the per-centage of organic matter; well waters contain less.

Relations of Lead to Air and Water.—(*a.*) Lead is not oxidated in dry air, or (*b.*) in pure water deprived of air. (*c.*) It is oxidated in water, other things being equal, in general proportion to the amount of uncombined oxygen in solution. (*d.*) When present in sufficient quantity, nitrates in neutral waters are to some extent reduced by lead. (*e.*) Both nitrates and chlorides promote the solution of some coats formed on lead.

(*f.*) Organic matter influences the action of water upon lead. If insoluble, it impairs the action by facilitating the escape of air; if soluble, by consuming the oxygen in solution, and by reducing the nitrates when present. The green plants, so called, and animalcula which evolve oxygen, are abundant in open waters in warm weather only, and of course when the capacity of water to retain air in solution is lowest; so that, although oxygen is produced in open waters by these microscopic organisms, it does not increase the vigour of their action upon lead.

(*g.*) Hydrated peroxide of iron (iron rust) in water is not reduced by lead. Hence may be inferred the freedom from corrosion of leaden pipes connected with iron mains, so far as the reduction of the pulverulent peroxide of iron may influence it.

(*h.*) Alkaline chlorides in natural waters deprived of air do not

* Rain-water is to some extent employed as a beverage. It is more nearly allied to waters derived from surface-drainage.

corrode lead. (*i.*) Salts generally impair the action of waters upon lead, by lessening their solvent power for air, and by lessening their solvent power for other salts.

A coat of greater or less permeability forms in all natural waters to which lead is exposed. The first coat (*j.*) is a simple suboxide absolutely insoluble in water and solutions of salts generally. This becomes converted in some waters into a higher oxide, and this higher oxide, uniting with water and carbonic acid, forms a coat (*k.*) soluble in from 7000 to 10000 times its weight of pure water. The above oxide unites with sulphuric and other acids, which sometimes enter into the constitution of the coat (*k.*); uniting with organic matter and iron rust, it forms another coat (*l.*), which is in the highest degree protective. The perfection of this coat, and of the first above mentioned, may be inferred from the small quantity of lead found in Croton water (New York) after an exposure in pipes of from twelve to thirty-six hours, and from the absence of an appreciable quantity in Fairmount water (Philadelphia) after an exposure of thirty-six hours, when concentrated to $\frac{1}{200}$ths of its bulk.

Method of determining small Quantities of Lead.—The recognition and quantitative determination of very minute quantities are not always without difficulty; where many and rapid determinations are required, the processes of gathering upon a filter, washing, drying, igniting and weighing consume far too much time, and are sometimes less accurate than other and more indirect methods.

That which I have employed is based upon the mode of analysing silver coin proposed by Gay-Lussac, and generally adopted at mints. The same general method has been extended by Gay-Lussac to ascertain the strength of alkalies and bleaching powder. It is employed with protosulphate of iron and subchloride of mercury for the latter purpose. It is the method of graduated solutions.

A gramme of lead in the form of the acetate (common sugar of lead), which contains 3 atoms of water, is dissolved in 100 grms. or parts of distilled water. This constitutes solution No. 1.

10 parts of this solution are diluted with 90 parts of water to make solution No. 2.

10 parts of solution No. 2, diluted with 90 parts of water, make solution No. 3.

In the same manner solutions No. 4, No. 5 and No. 6 are prepared.

10 parts of each solution are placed in corresponding test-tubes (about six inches long, five-eighths of an inch wide, and closed at one end), and hydrosulphuric acid transmitted through them, till the liquid, first blackened by the formation of sulphuret of lead, becomes clear.

Test-tube No. 1 contains one-tenth of a gramme of lead in the form of sulphuret—a black powder at the bottom.

Test-tube No. 2 contains one-hundredth of a gramme.

No. 3, one-thousandth.

No. 4, one ten-thousandth.

No. 5, one hundred-thousandth.

No. 6 yielded no precipitate without concentration.

Each succeeding precipitate in the series, setting aside a slight allowance to be made on account of solubility, was one-tenth as voluminous as the one above.

Having prepared this scale of quantities, it is required to determine the amount of lead in a given diluted solution. An experiment is made to ascertain if the quantity be large enough to give an immediate precipitate with sulphuret of ammonium. This being decided in the negative, 50 cubic centimetres or grammes of water (corresponding with 50 parts of the scale of solutions) are carefully evaporated to dryness and ignited in a small porcelain capsule, to expel any organic matter that may have been present, moistened with nitric acid, and then warmed, with the addition of acetic acid and water, till the volume becomes 10 cub. centim. A drop of acetate of potash is then added, and then hydrosulphuric acid gas transmitted through the solution.

A precipitate results, or it does not. If it does, to know its value or the amount of lead it contains, the scale is resorted to. Though it might rarely be possible to identify it with either one of two precipitates in the scale, there could be no difficulty in deciding between which two it should fall, or nearest to which one of two it should be placed.

If 50 cub. centim. thus treated yielded no precipitate, 100 cub. centim. were evaporated to dryness, and the residue similarly treated. If this failed, 500 cub. centim. were taken, and in some instances more, and the same course pursued.

It was natural to suppose that the presence of foreign bodies, such as occur in natural waters, might embarrass the precipitation. This led to the preparation of a series of graduated solutions of lead, with all the common salts occurring in waters, from the reagents in my laboratory. They were similarly treated with acetate of potash, free acetic acid, and a stream of hydrosulphuric acid; and though it was possible to see differences in the amounts of the precipitates, they fell very greatly within the differences between the successive members of the graduated series.

On the presence of Allantoine in Urine. *By* M. Wöhler.

The allantoic liquid of the cow is generally considered to be nothing more than the urine of the fœtus, and this liquid contains a peculiar substance, allantoine. It was therefore to be presumed that the same substance would likewise be found in the urine of the born animal; and, in fact, I have found it to be an essential and constant principle of the urine of the calf. It has only to be evaporated down to one-sixth of its volume to cause the allantoine to crystallize mixed with a considerable quantity of crystallized phosphate of magnesia. To purify and decolorize it, it is redissolved in boiling water, and the solution mixed with a little animal charcoal. The crystals thus obtained, although perfectly white, always affect a different form from that of ordinary allantoine, and which arises from

a foreign substance, which can only be removed by combining the allantoine with oxide of silver. On separation from this compound by hydrochloric acid, the allantoine from the urine of the calf does not differ from that obtained from the allantoic liquor or from uric acid either in form or composition. It is $C^8 H^{12} N^3 O^6$.

The urine of the calf is acid, and contains, besides the allantoine, uric acid and urea nearly in the same proportions as in the urine of man; but it contains no hippuric acid, an essential constituent of the urine of the cow, which is moreover alkaline and contains no allantoine.—*Comptes Rendus*, July 2, 1849.

Some Observations on Chloroform.
By Messrs. Soubeiran and Mialhè.

Two liquids are sold in commerce under the name of chloroform, which, although of very different origin, have nevertheless been hitherto considered as identical, and substituted one for the other. However, they exhibit some remarkable differences in their properties; the one derived from the action of hypochlorite of lime upon alcohol possesses all the characters which have been assigned by one of us to chloroform, and which we shall therefore call *normal chloroform*; the other, obtained by the action of hypochlorite of lime on pyroxylic spirit or methylic alcohol, differs so much from the first that we were induced to submit them to a careful comparative examination to ascertain the cause of this difference.

The chloroform from pyroxylic spirit, which we shall call for convenience *methylic chloroform*, although possessing the same physical appearances as the normal chloroform, has quite a different odour; it is not sweet and agreeable, but empyreumatic and nauseous. Its density is less than that of ordinary chloroform; the latter weighs 1·496, whilst the specific gravity of the former is only 1·413*. Its boiling-point likewise appears to be lower; and lastly, the inhalation of the methylic chloroform, far from being agreeable and pleasant, produces a general feeling of sickness, followed by a heaviness in the head, and sometimes by vomiting.

These differences led us to believe that they did not possess the same composition, or that the properties of one of them were masked by some foreign substance. On the first hypothesis, it might be imagined that the chloroform, which does not belong to the same chemical type as alcohol, and which is produced by the profound disturbance caused by the action of chloride of lime, might prove to be a different substance according as it resulted from the action upon alcohol which belongs to the ethylic series, or from the reaction on wood-spirit, which belongs to the methylic series. It might also happen that the difference was owing to a weaker or stronger

* We may observe that the density of chloroform, fixed by M. Liebig at 1·480, is too low; we have constantly obtained 1·496 at 54° for a perfectly pure chloroform. This difference undoubtedly arises from the presence of a foreign substance which had not been separated from the chloroform, as we shall presently show.

condensation of the methyle, supposed to exist equally in the two chloroforms. To decide this, we undertook some analyses, the result of which will be given subsequently. The second hypothesis supposes the identity of the chloroform, whether it has been formed from alcohol or from pyroxylic spirit; the difference in this case would arise from the presence of a foreign substance. This opinion is better founded; in fact, on attempting to rectify methylic chloroform by successive distillations over chloride of calcium, we found that the salt forming the residue retained after each distillation a certain quantity of a peculiar oil, which was easily isolated by washing with water. By repeated rectification, we were able to obtain a considerable amount of this oil, the proportion of which rose to as much as 30 grms. in 500 in some commercial chloroforms.

This new substance is liquid and of an oily consistence. At first yellowish, it is rendered colourless by a simple rectification; it has a very peculiar and very strong empyreumatic odour, similar to that possessed by the methylic chloroform; it is lighter than water; it began to distil at 185°, but gradually rose to 271°. This rise of temperature during the distillation evidently indicates a mixture of different compounds. It readily took fire, and burnt with a very intensely smoky flame. The presence of chlorine among the products of its combustion, indicated that this body formed a constituent part.

Although rectified several times, the chloroform which had yielded this oil still retained the characteristic empyreumatic odour. We therefore sought for some chemical reagent, which, without acting upon the chloroform itself, should either separate or destroy the oil it still contained. After some experiments, concentrated sulphuric acid appeared to us most suitable; it produced in the impure chloroform a brownish-red colour, which was the more intense the more oil was contained in the mixture. This colour, which it likewise produces in a far higher degree with the isolated oil, is due to its carbonization; so that on distilling impure chloroform with a certain quantity of concentrated acid, we succeeded in obtaining a product which was no longer coloured by this powerful reagent, and possessed no empyreumatic odour.

We were then able to analyse the chloroform thus purified, and to examine its properties compared with those of normal chloroform. Composition, boiling-point, density in the liquid state and in the state of vapour, were all found to be perfectly alike; and we were able to assure ourselves that there exists but one chloroform, and that that derived from wood-spirit does not differ in the least from the chloroform from alcohol when the precaution has been taken to separate the whole of the oil above-mentioned. However, it must be stated that the complete separation of this oil was not effected; there still remained a minute proportion, so small indeed as to have no influence either on the specific gravity or on the results of the analysis; but it was evident, from the odour which remained after evaporating a sufficiently large quantity of chloroform; and likewise the vessel used to take the density of the vapour, still perceptibly

retained the peculiar odour of this chlorinated methylic oil. It is almost impossible to remove the last traces of it; they resist the action of concentrated sulphuric acid even after long-continued contact.

There are therefore not two kinds of chloroform; but the presence of a peculiar oil, produced in the action of chloride of lime upon pyroxylic spirit, is the cause of the differences which they present at first sight. Having established this fact, we now inquired whether during the preparation of chloroform from alcohol a substance analogous to that just described was not produced. Our suppositions were confirmed by experiment. The crude chloroform was first washed with water, then with carbonate of soda, left for a long time with chloride of calcium to remove the water; and lastly, filtered and distilled in a glass retort in a water-bath. There remained in the retort an aromatic liquid, but of an odour different from that of chloroform; but the amount was very small, being not 40 grms. from 20 kilogrammes of chloroform.

This oil differs essentially from that obtained from the chloroform prepared with pyroxylic spirit; it is heavier than water, and has a peculiar acrid penetrating odour, totally different from that of the other. On attempting to determine its boiling-point, we found that, like the former, it consisted of a mixture of different compounds; for the thermometer, which stood at 154° at the commencement of the ebullition, rose to 243°, and the temperature would undoubtedly have risen still higher had a larger amount been at our disposal. All these compounds contain chlorine, as was evident from an examination of the products of their combustion. Although these different substances were not submitted to analysis, everything leads us to believe that they are intermediate in composition between chloroform and one of the known chlorides of carbon.

It is scarcely possible to decide by what reaction these chlorinated oils are produced, no organic analysis having been made; we may however observe, that in the preparation of chloroform from ordinary alcohol, the more chlorinated oil is formed the less chloride of lime is added to the mixture, or that the production of the substance is due to an excess of chlorine.

It results from what precedes, that the chloroform obtained from wood-spirit should not be employed for inhalation, it being impossible to deprive it entirely of its empyreumatic odour; it might be used for liniments, after having been previously rectified over sulphuric acid and chloride of calcium; but the necessity of these rectifications destroys the advantage which might arise from the substitution of pyroxylic spirit for alcohol.

The presence of the chlorinated oil, however small in quantity, even in the chloroform obtained from alcohol, has a very decided influence on the use of this substance. It is to it that must be most frequently attributed the sickness and vomitings caused by the inhalation of chloroform. It is therefore absolutely requisite to distil the chloroform, in order to separate the foreign substance which it contains; and this distillation should be stopped shortly before

the end of the operation, in order not to re-form the mixture. The oil contained in the residue then possesses in the highest degree the property of producing headache and giddiness; its action upon the system certainly requires that its physiological effects should be studied.

In conclusion, we may draw attention to a physical property of chloroform, which appears not to have been previously noticed; it is its solidification by spontaneous evaporation. When chloroform is poured upon a double filter of bibulous paper, a great portion of the liquid, from its heaviness and fluidity, quickly passes through the paper; whilst another portion, evaporating rapidly upon the margins of the filter, produces so much cold as to congeal it into white silky scales, which keep a few instants.—*Journ. de Pharm.*, July 1849.

Means of determining the Purity of the Otto of Roses.
By M. Guibourt.

The high price of this article renders it a matter of great importance to be enabled to decide upon its purity. The following means, if used in combination, will leave no doubt upon this point.

The physical characters can be but little depended upon; thus, the yellow colour with a tinge of green and its point of congelation may be readily imitated. Its odour also is so powerful, that a certain quantity of any other oil of a somewhat similar odour might be added without sensibly diminishing that of the otto. The manner in which it crystallizes is of a certain amount of importance. When, after having been liquefied by a gentle heat, it is allowed to cool slowly and at rest, it remains as it were transparent, in consequence of the thinness and the perfect transparence of its long and pointed crystals, which resemble the blades of daggers; and on varying their position as regards the light, these laminæ reflect all the prismatic colours. When the otto of roses has been adulterated with any uncrystallizable oil, which requires that its property of congealing should be imparted by the addition of spermaceti, it presents when solidified a number of fine needles, which however are not transparent, but render the mass uniformly semi-opake. But for this test to be of any value, the otto must be allowed to crystallize slowly and at rest; otherwise it becomes nebulous and opake, like that which has been adulterated.

The oil most frequently used for its adulteration is that of several species of *Pelargonium*. The oils derived from the different species cannot be all identical, since M. Recluz has described one which is solid, whilst that which is met with in commerce is always liquid. The oil which I employed for comparison is called oil of *Geranium*, and came from Nice. I also examined some oil of rose-wood, which was distilled at Paris some years ago, and some of that found in commerce. Three reagents will serve to distinguish the pure otto—iodine, nitrous acid vapour and sulphuric acid.

Test with Iodine.—A small quantity of iodine is placed in a small

glass vessel with a wide mouth; around it watch-glasses are arranged, each containing one or two drops of the oils under examination, and the whole is covered with a bell-glass. At the end of a few hours the vapour of the iodine is found to have condensed upon every part of the interior of the bell-glass and upon the glasses containing the oils; but the margin of the watch-glasses containing the substituted oils is much more coloured than that of the glass containing the otto; and when the former oils become brown, the latter retains its natural colour. After some hours the vessel containing the iodine may be removed; and then, the effect still continuing, the otto remains white, whilst the other oils become perfectly black. On exposing the watch-glasses to the air, the iodine which has condensed upon the margin of those containing the otto is volatilized, and the glass becomes almost colourless, whilst the others retain their black colour. I am satisfied that this test will serve, not only to determine the nature of the otto of roses, but also whether any oil of geranium or rose-wood is present in it or not.

Nitrous Acid Test.—For this I use a small glass vessel, placed upon a plate. 10 or 15 grms. of concentrated nitric acid are placed in it, and some copper turnings added. Around this, watch-glasses are placed, containing one, or *at the most* two drops of the oils, and the whole is covered with a flat bell-glass. In a few minutes the oil of rose-wood acquires a dark yellow colour; the otto acquires nearly the same colour; whilst the oil of geranium becomes of an apple-green colour, and retains it for some time.

This test will serve to distinguish the two oils when in a state of purity, and may even serve to recognise oil of geranium containing the otto, because of the yellow colour which it imparts to the latter; but it is evident that it cannot serve to determine the presence of the oil of geranium in the otto of roses.

Sulphuric Acid Test.—One or two drops of the oil to be tested is put into a watch-glass; the same number of drops of very concentrated sulphuric acid are added, and the two fluids mixed with a glass rod. All the oils are rendered more or less brown by this proceeding; but—

The otto of roses retains the purity of its odour.

The oil of geranium acquires a strong and disagreeable odour, which is perfectly characteristic.

The odour of the oil of rose-wood is increased, and becomes somewhat unctuous. It is not, however, characteristic.

The commercial oil of rose-wood acquires an odour distinctly like that of cubebs.

Of these three methods, that with sulphuric acid is by far the best for distinguishing the otto of roses from the oil of geranium, and for the recognition of the second in the former. The iodine-test is also very certain, but it requires considerably more time. The nitrous acid test will serve to recognise the two oils when not mixed, or even to detect the otto of roses in the oil of geranium; but not the latter when mixed with the former.—*Journ. de Pharm.*, May 1849.

On a Chromate of Copper and Potash. By A. Knop.

This compound, discovered by M. Knop, forms a pure light brown powder, iridescent in sunshine, and which consists of transparent, microscopic, six-sided plates. It is almost insoluble in water. In carbonate and caustic ammonia it dissolves with a deep green colour; and on the cooling of a hot saturated solution, a salt separates in shining green prisms, with a play of golden yellow, and which, according to the description, appear to be the chromate of ammonia and copper prepared by Malaguti by a different process.

This potash double salt is immediately formed when recently precipitated hydrated oxide of copper is mixed with a solution of bichromate of potash; it is likewise obtained when a solution of sulphate of copper is mixed with an excess of a solution of bichromate of potash, and then caustic potash gradually added. The precipitate is at first of a paler colour, but subsequently becomes darker and crystalline.

On ignition, the salt yields water and oxygen, and leaves a mixture of oxide of copper and oxide of chromium with neutral chromate of potash, which latter may at least be partially extracted by water. For analysis, the salt dried over sulphuric acid was dissolved in muriatic acid, the copper separated by sulphuretted hydrogen, and weighed in the usual manner as calcined oxide of copper. The liquid filtered from the sulphuret of copper was boiled to expel the excess of gas, and the oxide of chromium precipitated by ammonia. After it had completely separated by long boiling, it was collected on a filter, weighed after ignition, and calculated as chromic acid. The solution filtered from it was evaporated to dryness, and the salt heated in a platinum crucible to volatilize the chloride of ammonium; the potash was then weighed as chloride of potassium.

In three analyses, made with 1·478, 1·666 and 0·944 grm. of salt of different preparations, the following quantities were obtained:—

Chromic acid	43·549	42·665	43·261
Oxide of copper	36·814	37·135	35·916
Potash	13·735	13·834	14·000

These numbers corresponded for the anhydrous salt to the formula $KO, CrO^3 + 3CuO, 2CrO^3$. As the chromic acid in the chromate of copper is converted on calcination into oxide of chromium, it must lose 3 atoms of oxygen, corresponding to 6·732 per cent. From the difference in the loss by ignition the amount of water can be determined. 6·357 grms. salt lost on calcination 0·905 or 14·236 per cent. water and oxygen. A second experiment, with only 1·382 salt, gave 13·821 per cent. loss. Deducting the 6·732 oxygen from the first number, 14·236, leaves 7·504 for water, the oxygen in which is equal to that of the oxide of copper, and corresponds therefore to 3 atoms. According to theory the salt should lose by ignition 14·580 per cent. of water and oxygen, which comes sufficiently near to the amount found.

The unaltered salt consists therefore of $KO, CrO^3 + 3CuO, CrO^3$

+3HO, which would probably be more correctly expressed by (KO, CrO^3 +2CuO, CrO^3 +CuO, HO)+2HO. The corresponding per-centage composition is—

Chromic acid.....	43·878
Oxide of copper	34·579
Potash	13·695
Water	7·848

Liebig's *Annalen*, April 1849.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Preparation of a Glaze for Porcelain resembling Aventurine. By A. Wæchter.

According to Wöhler's examination, aventurine glass owes its golden iridescence to a crystalline separation of metallic copper from the mass coloured brown by the peroxide of iron.

In the aventurine glaze for porcelain a crystalline separation of green oxide of chromium from the brown ferruginous mass of the glaze produces a similar effect. I prepare this glaze as follows:—

31 parts of fine lixiviated dry porcelain earth from Halle,
43 ... ... dry quartz sand,
14 ... ... gypsum,
12 ... ... fragments of porcelain,

are stirred up with 300 parts of water, and by repeated straining through a linen sieve uniformly suspended in it, and intimately mixed. To this paste I add, under constant agitation and one after the other, aqueous solutions of

19 parts bichromate of potash,
100 parts protosulphate of iron,
47 parts acetate of lead,

and then add so much solution of ammonia that the iron is completely separated. The salts of potash and ammonia are removed by frequent decantation with spring water.

The baked porcelain vessels are dipped into the pasty mixture obtained as above described in the same manner as with other glazes, and then fired in the porcelain furnace. After this they appear covered with a brown glaze, which in reflected light appears to be filled with a countless number of little gold spangles.

A thin fragment of the glaze appears, under the microspope, by transmitted light, as a clear brownish glass, in which numerous transparent green six-sided prisms of oxide of chromium, and some brownish crystals, probably of oxide of chromium and peroxide of iron, are suspended. The oxide of chromium therefore separates, on the slow cooling of the glaze in the porcelain furnace, from the substance of the glaze—a silicate of potash, lime and alumina—saturated with the peroxide of iron, and shines through the brownish

mass with a golden colour. When the aventurine glaze is mixed with an equal amount of colourless porcelain glaze, the glassy mass no longer has a brown colour after the burning, but a light greenish-gray, and the eliminated crystalline spangles likewise exhibit in reflected light their natural green colour.—Liebig's *Annalen*, April 1849.

On Chicory-Coffee, its History, Manufacture, Adulterations, and means of detecting them. By A. Chevalier.

History and Manufacture.—The manufacture of a factitious coffee from the roasted root of chicory appears to have originated in Holland, where it has been practised for more than a century. It remained secret until 1801, when it was introduced into France by M. Orban of Liege and M. Giraud of Horning, a short distance from Valenciennes.

In a memoir upon coffee by M. Payssé, some details are given on the preparation of chicory-coffee in Holland. These were printed by Parmentier in the 'Annales de Chimie' for 1806, and are as follows:—

"The chicory for this purpose is collected in spring; the roots are conveyed to the manufactory, stripped of their leaves and washed to remove the soil*. They are cut into six parts, and then divided and dried. When dry, they are roasted in great cylinders like coffee. After the roasting, the chicory is reduced to a coarse powder.

"In Holland this chicory is then mixed in variable proportions with coffee; the resulting product is very bitter, which is considered by the common people to be a very salutary refreshment, which modifies the stimulant action of the coffee. Such a favourable idea has been formed of it, that of late this preparation has been employed alone, without any addition of coffee; and nevertheless it possesses no other virtue than that of colouring more or less readily the water in which it is boiled or infused, of communicating to the liquid the bitter taste of the extractive substances contained in chicory, and of being far less expensive than coffee."

M. Payssé adds, that "peas, lupins, beans, beet-root, carrot, &c. have been employed as a substitute for coffee."

The manufacture of chicory-coffee however remained for a long time stationary and of little importance; but for the last twenty years it has extended considerably, and has become an object of commerce of great importance. Till within the last few years it was carried on principally near Valenciennes; but since then manufactories have sprung up in several localities, especially at Arras, Cambray, Lille, Paris, Senlis in Normandy, Brittany and in England†.

The cultivation of chicory, to obtain the root for the purpose of converting it into coffee, has become a source of great prosperity

* The roots are now no longer washed, as this operation is said to injure their value.

† For the last two years very large quantities of dry chicory have been exported from France into England.

for these districts. The plant requires a deep soil of good quality, and well-prepared; the seed is sown in May, and the harvest takes place in October. Some time before collecting the roots, the leaves are mowed, and cows fed with them*. The roots are dug up with a spade, placed in heaps, and covered with straw to preserve them from frost.

The roots, thus collected, are cut at first longitudinally, and then transversely, in pieces from 5 to 10 centimetres in size; they are then carried into the drying chambers, which are heated with a kind of anthracite which produces no smoke. The roots are placed in layers of about 40 centimetres; they are frequently stirred to prevent them from burning and to facilitate the drying. Four such operations are made in about twenty-four hours. The roots dried by the above process are known by the name of *Cossètes*. They are kept in granaries; but in general sold almost immediately to the manufacturers, who roast them according to the demand. When the roasting is nearly complete, 2 per cent. of butter is added, and a couple of turns given to the roasting machine. This addition is made in order to impart lustre to the chicory, and to give it the appearance of roasted coffee. The substance is then emptied into iron vessels, and after cooling is crushed in vertical stone mills or between iron cylinders; it is then sifted, and during this operation a small quantity of a reddish colouring substance (*rouge brun de Prusse*) is added to give it the colour of coffee. The product is then weighed off, and sold in packets under a variety of names, but very rarely under its own; for instance, among others, *Mocha powder, Ladies' coffee, cream of Mocha, pectoral coffee, Chinese coffee, Tom Thumb coffee, Polka coffee and colonial coffee.*

We have stated that it forms a very important object of commerce; in fact, 12,000,000 lbs. are consumed in France, and a large quantity is exported. On consulting the tables of the commerce of France, it will be seen that from 1827 to 1836 there was exported from France 458,971 kilogrammes of chicory-coffee of the value of 321,282 francs; and since this period the amount has vastly increased.

Adulteration.—This substance is very frequently mixed with other ingredients, the means for detecting which consequently vary. We shall briefly notice them.

I. Brick-dust, ochre and earth may be detected by incineration and determining the amount of ash; 100 grms. of pure chicory-coffee furnish from 4 to 5 per cent. of residue; an excess would indicate fraud.

II. Adulteration with coffee-grounds. This is carried on upon a great scale in Paris. It is easily detected. A sample of the suspected chicory is dried in a water-bath, and a pinch thrown upon the surface of a glass of water; the chicory almost immediately absorbs the water and sinks to the bottom of the vessel, whilst the coffee-grounds remain on the surface.

III. Adulteration with roasted bread, dirt and remains from ver-

* It forms an excellent fodder; but when given alone, communicates a very disagreeable flavour to the milk of the animals.

micelli, &c. This adulteration is generally made with crusts of bread collected in the streets, crusts which are not always very clean. They are roasted or rather burnt in the oven, ground and mixed with the chicory-powder. This adulteration can be detected by iodine-water, as the product resulting from the decoction of pure chicory does not strike a blue colour.

IV. Adulteration with roasted acorns, which may be detected by iodine-water and by persulphate of iron, which in such a case strikes a black colour.

V. Adulteration with roasted corn, haricots and peas may be detected by means of iodine-water.

There is no method as yet known of detecting the adulteration by roasted beet-root and carrot.—*Journ. de Pharm.*, July 1849.

Mode of silvering Glass by the Employment of Gun-Cotton.

M. Vohl has recently discovered that a solution of gun-cotton in a caustic ley possesses in a high degree the property of precipitating silver from its solutions in the metallic form. In fact, on bringing gun-cotton into contact with a caustic ley of sufficient strength, the cotton will become dissolved in the ley, giving out ammonia with a considerable degree of heat, and producing a deep brown liquid, somewhat thick. On pouring an acid into this, a brisk effervescence is produced, carbonic acid and nitrous acid being disengaged.

The action of the gun-cotton in this instance shows that it is not simply dissolved, but undergoes decomposition, by which the atoms of oxygen in the nitric acid enter into combination with the atoms of carbon in the cotton, thus producing carbonic acid, which, as well as the nitrous acid produced by the nitric acid, combines with 1 part of potash. A fresh decomposition of nitrous salt by the potash, in the presence of hydrogenated substances, furnishes ammonia.

The most remarkable property of this alkaline solution is the following:—On pouring into it a few drops of a solution of nitrate of silver, and adding ammonia until the oxide of silver formed is redissolved (the mixture being slowly heated in a water-bath), the liquid will at a certain period assume a deep brown colour and effervesce, the whole of the silver being precipitated on the sides of the vessel. The mirror thus produced is much superior in brilliancy to those produced by means of ætherial oils or ammoniacal aldehyde; and the facility with which it is produced will doubtless render it of practical importance.

This property is not exclusively possessed by gun-cotton; it is found also in cane-sugar, sugar of milk, manna, gums, and other substances which may be rendered explosive by treating them with nitric acid. Nitropicric acid produces under the same circumstances a reflecting metallic surface; and it appears that this reaction takes place with all bodies which, when treated with nitric acid, do not furnish products of oxidation, but another series of bodies which admit of carbonic acid forming one of their constituent parts.—*Technologiste*; and Newton's *Journal*, May 1849.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

Researches on Piperine. By T. WERTHEIM.

THE experiments hitherto published relating to piperine are limited to some elementary analyses. It is however well known how variable and doubtful such results are, unless they are checked by decompositions and combinations, even in the hands of the most ingenious experimenters, in establishing the constitution of very complex organic compounds. The first object was to prepare a double salt with platinum. It was obtained in beautiful crystals of a splendid dark orange-red colour, belonging to the hemiorthotype system. To prepare it, a concentrated alcoholic solution of piperine, which has been repeatedly recrystallized, is mixed with a concentrated alcoholic solution of chloride of platinum, and the mixture, after the addition of concentrated muriatic acid, left for several days to spontaneous evaporation. In the course of twelve to twenty-four hours the first crystals make their appearance; they then gradually increase in quantity, and when sufficiently concentrated solutions have been employed, a very large amount is obtained. The crystals prepared in this manner are so large and compact, that they may be collected on a funnel with a narrow neck without loss, and freed from adherent mother-ley by rinsing with strong spirit. This double salt is very sparingly soluble in water; but it appears to experience a partial decomposition in contact with large quantities, muriatic acid being set free, and apparently unaltered piperine eliminated. It causes a strong burning taste upon the tongue, which probably arises from this decomposition. It is pretty readily soluble in cold alcohol, but far more so in boiling; on cooling, nearly the whole amount separates as a fiery orange-coloured crystalline powder. The chloride of piperine and platinum may be dried at 212° without alteration. At a little higher temperature it melts, and it is decomposed with considerable tumescence. It furnished on analysis the following results:—

Carbon.....	54·61	54·40	54·53	..	70 = 5250		54·46
Hydrogen....	5·48	5·40	5·26	5·05	38	475	4·93
Platinum	12·60	12·68	12·75	12·78	1	1233·3	12·79
Nitrogen	3·53	..	..	..	2	354·1	3·68
Chlorine	13·41	..	..	..	3	1328	13·77
Oxygen.....	10·37	..	..	..	10	1000	10·37

This per-centage composition leads therefore to the formula $C^{70}H^{37}N^2O^{10} + ClH + PtCl^2$, from which we immediately obtain for pure piperine the formula $C^{70}H^{37}N^2O^{10}$.

If we calculate the per-centage composition of piperine according to this formula, we have—

Carbon	74·29
Hydrogen	6·55
Nitrogen	5·01
Oxygen	14·15

If we compare these numbers with those obtained by Liebig, Pelletier, Regnault, Will and Varrentrapp, and quite recently by M. Laurent, a very considerable difference is immediately evident; but if we admit piperine to contain 2 equivs. water of crystallization, which as usual does not enter into the composition of the platinum double salt, a very satisfactory agreement with the numbers obtained by Regnault and Laurent results. The formula $C^{70}H^{37}N^2O^{10} + 2aq$ requires—

	Calculated.	Regnault.		Laurent.
Carbon	72·00	72·03	72·33	71·66
Hydrogen	6·69	6·72	6·84	6·66
Nitrogen	4·85	4·94	4·94	
Oxygen	16·46	16·31	15·89	

A comparison of these results will justify the above supposition; and the object in view did not appear to require further confirmation. I immediately proceeded to investigate the peculiar decomposition which piperine experiences at a high temperature in contact with fixed alkalies.

When an intimate mixture of piperine with 3 to 4 times its weight of a mixture of equal parts of soda and hydrate of lime is exposed in a retort in an oil-bath for some length of time to a temperature between 302° and 320°, a perfectly colourless oily liquid distils over in considerable quantity; and if the above-mentioned temperature has not been exceeded in the course of the operation, not a trace of ammonia is contained in the distillate. The oily product exhibits the following properties:—It has a peculiarly penetrating lasting odour; a very acrid burning taste, which when strongly diluted becomes extremely bitter. I have kept a large quantity of this oily body several months in a flask, which was frequently opened, without any apparent change; it has a strong permanent alkaline reaction; it produces no violet colour with a solution of chloride of lime. In short, it entirely corresponds in its properties with a substance recently described by Mr. Anderson by the name of *picoline*, with the exception of a single important reaction. When, for instance, a somewhat large amount of this oily product is mixed with nearly an equal quantity of albumen, this is coagulated after some time, which is not the case with picoline; but it frequently requires more than a quarter of an hour.

To ascertain the composition of this substance, the double salt with platinum was analysed. It was prepared by dissolving the original distillate in water containing sulphuric acid, avoiding an

excess of acid; the solution was then evaporated to dryness in the water-bath, and the residue dissolved in absolute alcohol, in order to remove any trace of ammonia that might possibly be present. The alcoholic solution was now mixed with an excess of muriatic acid, and an alcoholic solution of chloride of platinum added, when an abundant precipitate of the double salt, in the form of exceedingly delicate feathery crystals of an orange colour, resulted. When very concentrated solutions are employed, the entire liquid solidifies to a paste. Washed with alcohol and æther and dried at 212°, this compound furnished the following results on analysis:—

Carbon	23·39	..	12 =	900	24·07
Hydrogen	2·94	..	8	100	2·67
Platinum.....	32·30	32·95	1	1233·3	32·94
Nitrogen.....	..	..	1	177	4·73
Chlorine.....	..	..	3	1328	35·59

The formula of the chloroplatinate of this volatile base is $C^{12}H^7N + ClH + PtCl^2$. There can consequently be no doubt that the volatile base obtained by the above process from piperine is in fact picoline. In a notice communicated on this subject, before Mr. Anderson had published his beautiful investigations on this new base, I had considered it to be aniline, judging solely from the above-mentioned numerical results. The different reaction above-mentioned may possibly be explained from the circumstance that a considerable quantity of the base and of albumen were employed, and the result observed after the lapse of at least a quarter of an hour.

Having established the composition of the volatile product, I now proceeded to examine the solid residue in the retort. In the course of the operation the mixture assumes a dark cinnamon-brown colour. As long as heat is applied, it is of a soft consistence, as the piperine melts at this temperature; when cold, it forms a hard agglutinated mass. If the heating has been continued sufficiently long, this mass contains but very little unaltered piperine, but a large amount of a new product, which may be obtained pure by treating the pulverized mass repeatedly with large quantities of water, which must not be hot; otherwise the particles cake together, and the water can no longer penetrate the mass.

After having removed in this manner the excess of the hydrate of soda, the dried residue is again pulverized, and digested several hours with cold alcohol to remove every trace of piperine; the residue is then mixed with hot water to which an excess of hydrochloric acid has been added, and the acid liquid boiled for some time. The acid should be added very gradually in order to avoid a too violent evolution of the carbonic acid. The muriatic acid dissolves the hydrate of lime contained in the residue, which when freed from lime becomes suspended in the liquid in the form of brown flakes; but in proportion as the boiling is continued, the brown flakes unite, and form a homogeneous, soft and compact mass of a dark brown colour, and the liquid becomes perfectly clear. If the soft cake of resin be removed from the hot liquid, and rinsed

for a few moments with a little cold water, it immediately becomes perfectly brittle, and can be pulverized without difficulty when dry. It still contains a considerable quantity of hydrate of lime, and must consequently be again digested with dilute muriatic acid. When the resin has been treated in this way two or three times and dissolved in boiling absolute alcohol, the cold solution is carefully mixed with small quantities of water until a slight milkiness appears. When this point has been carefully preserved, the liquid may be kept for several days without depositing the slightest precipitate; but as soon as a couple of drops of muriatic acid are added to the liquid, the most complete precipitation immediately results. The precipitate is of a delicate yellowish-brown colour and very bulky. When collected upon a filter, washed with cold water, and dried at 212°, it forms a soft, pale yellow, perfectly tasteless powder, and is so highly electrical that on reducing it to powder it gives off a considerable quantity of dust. When the precipitate has been dried at the ordinary temperature *in vacuo*, it possesses this electrical property in a less degree. On analysis it furnished—

Carbon.....	73·56	74·17	128	= 74·02
Hydrogen	7·00	6·86	67	6·45
Nitrogen	4·08	4·08	3	4·09
Oxygen	15·36	14·89	20	15·44

The empirical formula to which these results lead appears at first sight not to stand in any very direct relation with that of piperine; but if the formula of the latter be doubled and the formula of picoline be deducted from it, precisely the same group of atoms is arrived at:—

2 equivs. piperine ..... = $C^{140}H^{71}N^{4}O^{20}$
1 equiv. picoline..... = $-C^{12}H^{7}N$
= $C^{128}H^{67}N^{3}O^{20}$

This remarkable coincidence is readily explained by supposing the atom of piperine to be formed of two groups, of which the one is represented by the formula of picoline, $C^{12}H^{7}N$, and the other by $C^{58}H^{30}NO^{10}$:—

Piperine, $C^{70}H^{37}N^{2}O^{10} = C^{12}H^{7}N + C^{58}H^{30}NO^{10}$.

According to this view piperine would consist as it were of a saline compound, and the action of the soda-lime might be explained as follows:—

In the action of 1 equiv. hydrate of soda upon 2 equivs. piperine, 1 equiv. of the latter is decomposed. The soda takes the place of the separated picoline, and the soda compound formed immediately unites with 2 equivs. piperine to a kind of double compound:—

Before the experiment.

$$\begin{matrix}(C^{58}H^{30}NO^{10} + \text{picoline})\\(C^{58}H^{30}NO^{10} + \text{picoline})\end{matrix} \text{ and } NaO.$$

After the experiment.

$$\left(\begin{matrix}(C^{58}H^{30}NO^{10} + NaO)\\(C^{58}H^{30}NO^{10} + \text{picoline})\end{matrix}\right) \text{ and picoline.}$$

This double salt, which we must imagine to be contained in the residue immediately after distillation, is decomposed on treatment with muriatic acid, which seizes the soda, leaving behind a kind of acid salt, in which for 1 equiv. picoline 2 equivs. of the electro-negative group are contained, *i. e.* $2(C^{58}H^{30}NO^{10})+C^{12}H^{7}N$. The empirical expression for this formula is $C^{128}H^{67}N^{3}O^{20}$, which agrees perfectly with the analysis of the product above-described. It was however found impossible to prepare this hypothetical double compound. Most probably the soda is contained in it in such feeble union that it experiences a gradual decomposition by the action of water. We are far from thinking that piperine should be viewed, in consequence of these experiments, as a true salt; but our assumption, that in piperine an electro-negative group is contained by the side of a basic group, may perhaps explain the indefinite character of piperine as a base, and its exceedingly weak affinity for the strongest acids. It is well known that it was long doubtful whether piperine should be enumerated among the alkaloids.

It results from this explanation of the process of decomposition, that only the half of the picoline supposed to be contained in the piperine is obtained under the circumstances above-mentioned.

It now appeared interesting to ascertain whether the decomposition might not be carried further by raising the temperature, the 2 equivs. picoline set at liberty, and perhaps the simple electro-negative group $C^{58}H^{30}NO^{10}$ obtained. It was found that the amount of produce might be considerably increased by raising the temperature of the oil-bath above 392°; but at this temperature a considerable quantity of ammonia passes over with the picoline. In the aqueous extract of the residue in the retort a peculiar substance is held in solution by the free alkali, which is precipitated on supersaturating the liquid with muriatic acid in yellow flakes; the amount obtained however was very small. This substance contains no nitrogen. It furnished on analysis—

Carbon	71·41	58	71·45
Hydrogen	5·65	27	5·54
Oxygen	22·94	14	23·01

According to this analysis, which was made with the greatest care as there was not material for a second, the composition of the substance produced by this further decomposition can be expressed by the formula $C^{58}H^{27}O^{14}$. It is impossible therefore to obtain the group $C^{58}H^{30}NO^{10}$, at least according to the plan followed; but if we compare the two groups, we find that they stand in a very simple relation, for $C^{58}H^{27}O^{14}=C^{58}H^{30}NO^{10}-H^{3}N+O^{4}$. This new substance consequently has been formed directly from the electro-negative group of piperine by the separation of 1 equiv. ammonia and the assimilation of 4 equivs. oxygen.

The rational formula, $C^{58}H^{30}NO^{10}+C^{12}H^{7}N$, which we have developed for piperine from the previously enumerated facts, may be essentially modified; for instance, admitting in this substance, as a salt of picoline, 1 equiv. of constitutional water, as generally occurs

in all the true salts of ammonia and the analogous bases, we obtain $C^{58}\ H^{29}\ NO^9 + C^{12}\ H^7\ N + HO$. The number of equivalents of hydrogen in the electro-negative group is by this change rendered exactly half that of the carbon equivalents; and the acid substance now appears as an oxide of a compound carbohydrogen.

If we attempt to apply this mode of conceiving the nature of piperine to the beautiful results with which Wöhler and Blyth have enriched our knowledge respecting narcotine, some extremely simple relations between this base and the two new bases which those chemists discovered, cotarnine and narcogenine, instantly present themselves. In the earlier notice above-mentioned we just pointed to these relations; since then M. Laurent has arrived at conclusions, which are in many respects analogous, by reflections of a very different kind and by ingenious combinations. We shall assume as the basis of our consideration the formula which Wöhler advanced for cotarnine, with the slight alteration of deducting from it 1 equiv. hydrogen. Now if we deduct this formula $C^{26}\ H^{12}\ NO^5 + 1$ equiv. water from the formula of narcotine, $C^{46}\ H^{25}\ NO^{14}$, we obtain the expression $C^{20}\ H^{12}\ O^8$. If we further admit these two groups in narcotine to be combined in a similar manner as in piperine, forming a kind of salt in which cotarnine would represent the base and the other group the acid, and starting from this assumption take into consideration the formula of narcogenine, we instantly discover a remarkably simple relation. If we add, for instance, to the formula of narcotine the elements of 1 equiv. cotarnine + 1 equiv. water, the sum is the formula of narcogenine doubled :—

$$\begin{aligned} &C^{46}\ H^{25}\ N\ O^{14} = 1 \text{ narcotine.} \\ +\ &C^{26}\ H^{13}\ N\ O^{6} = 1 \text{ cotarnine} + 1 \text{aq.} \\ \hline = &C^{72}\ H^{38}\ N^2\ O^{20} = 2 \text{ narcogenine.} \end{aligned}$$

We do not think that this remarkable coincidence can be at all viewed as accidental, and do not hesitate to deduce from thence the following conclusions :—

1. The composition of narcotine is expressed by the following rational formula,—

$$(C^{20}\ H^{12}\ O^8) + (\text{cotarnine} + \text{aq}),$$

i. e. narcotine is the neutral pseudo-salt of cotarnine and of the above bracketed electro-negative group.

2. The atomic weight of narcogenine must be doubled. Narcogenine then acquires the following rational formula,—

$$(C^{20}\ H^{12}\ O^8) + 2(\text{cotarnine} + \text{aq}),$$

i. e. narcogenine is the corresponding basic pseudo-salt.

It results directly from the second conclusion that the atom of the chloroplatinate of narcogenine must be doubled; the atom of this compound would then contain 2 equivs. chloride of platinum. This might at first sight appear anomalous; but it needs merely a glance at the rational formula which we have advanced for narcogenine to remove this apparent anomaly.—Liebig's *Annalen*, April 1849.

On the Action of Hyposulphite of Soda upon the Chloride of Antimony in the presence of Water. By A. Strohl.

Having let fall some drops of hyposulphite of soda upon a table which happened to be moistened with a little chloride of antimony, I was struck with the beautiful red colour which was produced in the course of a little time. Curiosity led me to attempt to produce this colour upon a greater scale, in order to ascertain how it is formed and its composition. My efforts were perfectly successful. A slight excess of hyposulphite of soda is mixed with chloride of antimony and water. The reaction takes place very slowly in the cold, but instantly on boiling; the product is allowed to deposit, the liquid decanted, the precipitate collected on a filter, washed with cold water and dried at a gentle heat.

This substance forms an excessively fine crimson-red powder of a velvety appearance; it has great resemblance to mineral kermes, and is not altered by the air or light. Under the influence of heat it behaves exactly like that substance; its colour becomes darker and darker, and it finally fuses to a black mass, which is a kind of crocus. Hydrochloric acid dissolves it with disengagement of sulphuretted hydrogen and a slight deposit of sulphur; tartaric acid deprives it of a large quantity of oxide of antimony. These general properties led me to consider the substance as an oxysulphuret, the production of which probably takes place as follows:—

2 equivs. of chloride of antimony are converted under the influence of water into insoluble oxychloride and hydrochloric acid; the hydrochloric acid reacts upon 3 equivs. of hyposulphite of soda, displacing 3 equivs. of hyposulphurous acid, which I represent, according to the views of M. Persoz, by ($SO^2 S$), *i. e.* as sulphuric acid in which 1 equiv. of oxygen is replaced by 1 equiv. of sulphur, and which has been termed on that account sulphosulphuric acid. [The following reaction furnishes a new proof in favour of that assertion.] The 3 equivs. of sulphosulphuric acid react in their turn upon the precipitated oxychloride of antimony. The 3 equivs. of sulphur combine with the radical of the chloride forming sulphuret of antimony ($Sb^2 S^3$), whilst the 3 equivs. of chlorine of the chloride have an oxidizing action, and convert the sulphurous into sulphuric acid. The sulphuret of antimony combines in the nascent state with the liberated oxide of antimony, forming the new oxysulphuret in question ($Sb^2 S^3 + Sb^2 O^3$):—

$2(Cl^3 Sb^2 + aq) = Cl^3 Sb^2 + Sb^2 O^3 + Cl^3 H^3$

$+ 3(SO^2 S + NaO) = (Sb^2 S^3 + Sb^2 O^3)$ insoluble, $Cl^3 Na^3 + 3SO^3$ soluble.

It is seen therefore that the reaction takes place between 2 equivs. of chloride of antimony and 3 equivs. hyposulphite of soda with the presence of water; and that, on the one hand, insoluble oxysulphuret of antimony is formed, and on the other, a mixture of chloride of sodium and sulphuric acid. It is also seen why a slight excess of hyposulphite must be employed, as with an excess of chloride the product is mixed with some oxychloride; in the other case it is

mixed with a little sulphur, produced by the spontaneous decomposition of the excess of hyposulphurous acid. However, this admixture is less important.

To obtain a product without mixture, exactly 2 equivs. of solid chloride of antimony and 3 equivs. of pure crystallized hyposulphite of soda should be employed. This nearly corresponds to the following proportions:—

Crystallized hyposulphite of soda	60 parts.
Solid chloride of antimony	50 ...
Distilled water.....	500 ...

To confirm this theory, I analysed the product. 5 grms. of substance, treated with a mixture of pure nitric acid and chlorate of potash, is converted into insoluble antimonious acid (Sb^2O^4); the whole of the sulphur is oxidized and converted into sulphuric acid. The filtered liquid furnished with chloride of barium 5·20 grms. sulphate of baryta, which represent 2·65 grms. sulphate of antimony. The formula $Sb^2S^3 + Sb^2O^3$ requires 2·69 grms. I propose to call this new substance *cinnabar of antimony*, from its colour, or normal oxysulphuret of antimony.—*Journ. de Pharm.*, July 1849.

On the Constitution of the Basic Nitrate of Bismuth. *By* H. Becker.

As different statements exist with respect to the composition of the *Magisterium bismuthi*, the author has been induced to make it the subject of fresh investigation.

The salt which separates immediately on mixing neutral nitrate of bismuth with water in the cold always possesses, according to the author, the same properties and the same composition whether a crystallized salt of bismuth has been used or a very acid solution. The precipitate which is produced by the addition of metallic bismuth to a concentrated solution of the nitrate is likewise identical with this basic salt. It always contains, as stated by Dulk, 1 equiv. of oxide of bismuth, 1 equiv. nitric acid, and 2 equivs. water. The analyses, in which the oxide of bismuth and the nitric acid were determined directly and the water calculated from the loss, furnished—

Oxide of bismuth..	77·33	77·51	77·47	1	= 76·65
Nitric acid	17·20	17·23	17·09	1	17·53
Water	5·47	5·26	5·44	2	5·82

At 212° this salt loses, as stated by Heintz, half its water.

When recently precipitated, this salt is dissolved in considerable quantity by water, especially if it contain nitric acid. If, therefore, after precipitating this basic salt, the liquid is mixed with a considerable amount of water, the precipitate is entirely redissolved; but after some time, which varies with the quantity of acid and the temperature, a basic salt separates. If the solution contain free nitric acid and the water added was cold, the compound $5BiO^3 + 4NO^5 + 9aq$ is formed, which according to Becker is the real *Magisterium*

bismuthi; as even by the original prescription, according to which the precipitate formed in an acid solution of bismuth upon the addition of water should be washed on the filter with water, the same salt is obtained, this change occurring on the filter with loss of acid; in this operation however a portion of the precipitate dissolves, and separates again from the filtered liquid after standing for some time. The decrease in the precipitate during the washing is owing more to the circumstance, that the precipitated salt with 1 atom of acid forms extremely delicate and light laminæ, whilst the *Magisterium* consists of thick short prisms. To prepare the basic nitrate therefore without any loss, it is advisable not to wash the precipitate produced by water upon the filter, but to decant the acid solution and then add a quantity of water. Its composition is—

	Found.			
		Herberger.		
Oxide of bismuth ..	79·85	80·18	79·7	5 = 79·91
Nitric acid	14·52	14·58	14·4	4 14·62
Water	5·63	5·26	5·9	9 5·47

As is seen, the analysis of Herberger agrees with this formula, although he deduces from it the formula $4BiO^3, 3NO^5, 9HO$.

Magisterium bismuthi does not dissolve perceptibly in cold water; it is however deprived of acid and a little oxide of bismuth; hot water changes it into a dirty white heavy powder. The powder which remained after long ebullition still contained 1 per cent. of nitric acid, which could not be completely removed by water.

The same proportion of acid and base, but with more water, was found in a salt, which separated, on evaporating a concentrated solution of bismuth at a high temperature, in white crystalline crusts, which on pressure between paper crumbled to a shining, crystalline, very hard powder. Its composition is—

Oxide of bismuth	78·49	5 =	78·48
Nitric acid	13·96	4	14·36
Water	7·55	12	7·16

The products which are obtained from the first precipitated salt with one atom of acid by a different treatment are quite distinct from the above. When, for instance, it is heated with water in the presence of free acid, or an acid solution of bismuth is poured into hot water, a white very loose powder is obtained, which is decomposed more rapidly by water than the basic nitrate, and possesses the following composition:—

Oxide of bismuth	80·19	80·29	6 =	80·16
Nitric acid	15·62	15·24	5	15·27
Water*	4·19	4·47	9	4·57

If this salt is washed with water until what passes through has no longer a strong acid reaction, the residue consists of prisms of far

* The composition of this precipitate differs evidently very slightly from that of the *Magisterium bismuthi*, and this may possibly be owing to the length of the washing.

greater size; and when dry forms a heavy dirty white powder, which possesses the formula $4BiO^3, 3NO^5 + 9HO$, and is consequently identical with the *Magisterium bismuthi* prepared according to Duflos's process.

Lastly, when the salt with one atom of acid, freed from all adherent acid liquor, is treated with pure water, it dissolves almost entirely. After a short time a milky liquid is obtained, from which in the course of time, a white amorphous powder is deposited, which is represented by the formula $5BiO^3, 3NO^5, 8HO$. This salt may be formed, together with *Magisterium bismuthi*, when too much water is used, and the acid liquor is for the greater part removed.—Liebig's *Annalen*, lxviii. p. 282.

Researches on the Composition of Honey. By M. Soubeiran.

The honey of bees contains two different sugars, the one solid, the other liquid. The former has been considered as identical with the granular sugar, which is deposited in the course of time from the syrup of the grape or from the syrup of cane-sugar altered by acids. With respect to the liquid part of honey, it has been little examined. M. Biot however has ascertained that it consists of a sugar which turns the rays of polarized light to the left.

The experiments contained in this memoir show that honey contains three distinct sugars,—first, the granular sugar or glucose of chemists; another sugar, with right-handed rotation, and which is alterable by acid; and lastly, a sugar the rotatory power of which is exerted towards the left, but with an energy almost double that of the sugar acted upon by acids.

I found the sugar possessing a right-handed rotation, and which is capable of being altered, in ordinary honey; but it is especially abundant in the liquid honey contained in the cells of the comb. The proportion is so great, that a solution of this honey which had a deviation of $+0{\cdot}96$ acquired, after the action of acids, a rotation in the opposite direction equal to $-13{\cdot}78$. I have named *liquid sugar of honey* the liquid portion which can be extracted from honey by pressure. My experiments were made upon a sugar which had been extracted in 1841, and which has kept to this day without experiencing the least change or exhibiting any sign of crystallization. This circumstance alone would suffice to distinguish it from the sugar altered by acids, which would soon have solidified into a mass of granular sugar. The liquid sugar of honey presents however a great number of characters which belong to cane-sugar altered by acids. Like it, it is uncrystallizable, and may be reduced to the state of barley-sugar, transparent and solid, but which melts with great facility; again, it resembles it in being very sensitive to the action of alkalies, and is readily destroyed by their influence. The two sugars have the same chemical composition, and enter into combination with the alkalies. Thus the totality of these characters would tend to confound these sugars; but they are distinguished

almost immediately by the absolute impossibility of converting the liquid sugar of honey into granular sugar, and by a very great difference in the rotatory power, which is nearly double in the liquid sugar of honey.

The absolute rotatory power of this liquid sugar at the temperature of 55°·4 F. for the red ray and for a length of 100 millimetres, was found equal to $-33°{\cdot}103'$, whilst that of sugar changed by acids was found under the same circumstances merely $=18°{\cdot}933'$. The liquid sugar of honey retains the rotatory power to the left, even after it has been brought to the solid state; it is one of a very small number of bodies in which this peculiarity has been observed.

The third sugar which forms part of the honey is distinguished from the granular sugar from its being altered by acids, and from the liquid sugar in possessing a rotation to the right. Its amount, which is pretty considerable in the liquid honey of the combs, diminishes in time, and may even disappear entirely in solidified honey.

I have limited myself at present to the establishing the facts as they result from observation; it is my intention to submit the honey of the combs to careful investigation, and also to inquire into the history of the curious transformation of the liquid into solid honey. Some experiments, which are not yet completed, promise to throw considerable light upon these phænomena and some facts of the same class which have already been published by M. Dubrunfaut. —*Comptes Rendus*, June 25, 1849.

Researches on Quinoidine and β-Quinine.

By J. Van Heijningen.

The following investigation was made with commercial quinoidine obtained in Holland. It is entirely soluble in acids and alcohol; but leaves in æther a residue from 12 to 15 per cent., according to the different kinds. It neutralizes acids, and burns with an agreeable odour, leaving scarcely any residue. Elementary analysis of the entire mass furnished dissimilar results, the carbon and nitrogen being higher (as much as 1 per cent.) in proportion to its greater solubility in æther. This quinoidine consists of a mixture of at least four to five substances: viz. 1st, *quinine* (the α-quinine of the author); 2nd, *cinchonine*; 3rd, a base of very peculiar properties, which the author calls *β-quinine*; and 4th, of a *resinous* colourless substance, which however readily becomes brown in the air. The quinoidine was treated in three different manners.

I. *Treatment.*—100 grms. of quinoidine were exhausted with as little æther as possible, and the brownish-yellow solution separated from about 14 grms. of a blackish-brown residue. The solution is decolorized with animal charcoal or the æther first removed by distillation, the residue dissolved in dilute sulphuric acid, and this solution treated with animal charcoal. The decolorized liquid is precipitated with ammonia, and the washed precipitate dissolved in

æther. The ætherial solution obtained in either way is mixed with one-tenth its volume of alcohol of 0·833 spec. grav., and left to evaporate spontaneously in a cool place. When the greater portion of the liquid has evaporated, a considerable amount of crystals of β-quinine have separated, which were purified by washing with alcohol.

The alcoholic liquid decanted from the β-quinine was, after further evaporation, accurately saturated with sulphuric acid, and the remainder of the alcohol removed by evaporation. On cooling, crystals of β-quinine, having great resemblance to the sulphate of quinine, separated from this solution. The mother-ley furnished a further quantity of these crystals, which were mixed with crystals of the ordinary sulphate of quinine and a dark brown colouring substance.

All the crystals of β-quinine are collected and purified by recrystallization from hot water. The ordinary sulphate of quinine is separated by dissolving the crystals in cold water with the assistance of a few drops of sulphuric acid, precipitating the solution with ammonia, carefully washing the precipitate, and dissolving it after desiccation in alcohol of 0·833 spec. grav. On slow evaporation, the β-quinine crystallizes, whilst the α-quinine remains dissolved in the alcohol.

The dark brown resinous residue left untouched by the æther is dissolved in dilute sulphuric acid, decolorized with animal charcoal and precipitated with ammonia; the dry precipitate is dissolved in hot alcohol, and set aside to crystallize; it is this portion of the quinoidine which contains the cinchonine, which now gradually separates, whilst the brown colouring substance remains in solution.

II. *Treatment.*—100 grms. of quinoidine were dissolved in æther, the solution decolorized with animal charcoal, and the æther removed by careful distillation. The residual yellow resinous substance was accurately neutralized with dilute sulphuric acid, and the solution evaporated at a gentle heat, when a quantity of crystals separated on cooling.

These crystals were considered by Winckler to be ordinary sulphate of quinine, but this is an error; they are sulphate of β-quinine with a slight admixture of the former. The liquid separated from these crystals is concentrated until no further crystals separate, then dissolved in water and decolorized. According to Winckler, ammonia precipitates from it pure quinoidine or amorphous quinine.

But if this precipitate, after having been dried, is dissolved in æther to which a little acid has been added, and the solution is left to evaporate spontaneously in a cool dry place, some more crystals of β-quinine are obtained from it. The separated liquid is saturated with dilute sulphuric acid, the alcohol evaporated. There is obtained on cooling, as in the first method, a further large amount of sulphate of β-quinine; the remainder of the liquid at last solidifies to a paste of crystals.

According to this method, therefore, the same results are obtained as according to I., only with greater loss of material and time; for

the β-quinine is decomposed, under the influence of acids and heat, apparently by the presence of a colourless substance, which becomes brown and resinous in the air; so that it requires to be frequently decolorized, because these products of decomposition prevent the crystallization of the β-quinine still in solution.

III. *Treatment.*—100 grms. quinoidine were dissolved in dilute muriatic acid, the solution decolorized with animal charcoal and precipitated with ammonia. The white flocculent precipitate soon contracted into a resinous cake, which became brown in the air. The well-washed and dried precipitate was dissolved in alcohol of 0·833 and concentrated; the dark solution deposited on cooling crystals which appeared to be pure cinchonine; after further evaporation the thick liquid was treated with æther, when more, nearly pure cinchonine was obtained. The æther is removed by cautious distillation; the residue in the retort saturated carefully with sulphuric acid, when, on evaporating the solution, a large amount of β-quinine separates. The mother-ley is evaporated until no more crystals are deposited on cooling; it is then dark brown, and water precipitates from it a blackish-brown resinous substance. After the separation of this substance, the liquid is again precipitated with ammonia, and the precipitate dissolved in sulphuric acid. This last precipitation renders the evaporation of a large amount of liquid unnecessary, in which operation it would again become brown. The concentrated sulphuric solution gave on cooling crystals which consisted of a mixture of α- and β-quinine, which were separated in the manner above described. The liquid separated from these crystals was decolorized, precipitated by ammonia, the dry precipitate dissolved in æther, and treated as above.

Of these three modes of treatment, the first is certainly preferable, because a larger portion of the β-quinine is separated before acids and heat are applied. Pure β-quinine is as little changeable as α-quinine or cinchonine; it is only when mixed with other substances that it is so readily decomposed. If Winckler's pure quinoidine be kept for some time even in closed glass vessels, it becomes darker at the surface; and this takes place very rapidly if the pale yellow-coloured quinoidine is kept fused for a couple of hours in a water-bath, or when it is dissolved in alcohol or in dilute acids and heated; the colour then soon passes from a pale yellow into a dark brown.

When the colourless quinoidine of Winckler is dissolved in dilute sulphuric acid so as to form a perfectly neutral solution, and it is then heated for a few hours until the colour has become dark brown, few or no crystals of β-quinine separate on cooling. From such a solution water throws down a black precipitate, and the liquid becomes lighter. If the solution is now precipitated with ammonia, and the precipitate dissolved in warm dilute sulphuric acid so as to form a perfectly neutral liquid, a large quantity of crystals of β-quinine separate; it is therefore beyond all doubt that the presence of the black substance prevents the separation of the crystals.

The fourth substance, above-mentioned, can also be obtained colourless; it exists in the colourless state in the mixture with β-quinine, which Winckler calls pure quinoidine; in commercial quinoidine, it is present partly in the colourless state and partly of a brown colour, having been oxidized by the oxygen of the atmosphere. This product of oxidation would consequently form the fifth constituent of quinoidine. However, from the author's experiments nothing accurate can be stated of this substance, except that it is not an alkaloid, and is probably free from nitrogen; for the following analyses correspond to a mixture of the cinchona-alkaloids with a non-nitrogenous substance. I., II. are the found results with quinoidine; III. the calculated composition of quinine; IV. the calculated composition of cinchonine:—

	I.	II.	III.	IV.
Carbon	72·81	72·69	74·1	78·0
Hydrogen	7·30	7·30	7·4	7·8
Nitrogen	8·47	8·89	8·6	9·1

It should be observed that the β-quinine in the anhydrous state has the same composition as α-quinine. It results then from the above numbers, that the quinoidine of commerce must contain, besides α- and β-quinine and cinchonine, a fourth substance containing less carbon and hydrogen than quinine. In order to obtain further information on this point, the substance considered by Winckler to be pure quinoidine, but which is a mixture of β-quinine and of a substance which turns brown in the air, was analysed. On drying, the colourless substance became brown, and consequently the analysis has no value in reference to its composition; but it is only intended to prove that the supposed amorphous quinine cannot have the composition of quinine. A sample of this substance, dried at 266°, and which had become brown, furnished on analysis 74·441 carbon, 7·491 hydrogen, 7·466 nitrogen, and 10·602 per cent. oxygen. The quantities of hydrogen and carbon are the same, but the amount of hydrogen is 1 per cent. less than in quinine.

It is evident therefore that the so-called amorphous quinine, even when prepared according to the method directed by Winckler, is still a mixture.

β-quinine, $C^{20}H^{12}NO^2+2HO$.—It will be seen from the following, especially from the nature of the salts, that this is a very peculiar alkaloid, which in the anhydrous state has the same composition as anhydrous α-quinine; but it decidedly differs from it in the hydrated state; the α-base combines with 3 equivs. water, the base β with only 2. In some salts the latter likewise contains less water of crystallization than α-quinine. When prepared according to the methods previously described, it has the following properties:—It crystallizes from ætherial hot alcoholic solutions in large, transparent, klinorhombic prisms, which become white and opake in the air, without however falling to powder. At 320° it melts to a colourless liquid, which forms on cooling a transparent resinous mass; when heated upon platinum foil, it burns with an agreeable

smell, resembling the odour of Melilotus. At 46°, it dissolves in 1500 parts water, in 4·5 parts of absolute alcohol and 90 parts of æther, whilst of boiling alcohol it requires only 3·7 parts and of boiling water 750 parts; from which solutions it again separates for the greater part on cooling. In this respect it differs essentially from α-quinine and from cinchonine.

The cold aqueous solution has a feeble alkaline reaction, is rendered turbid by alkalies, and furnishes a white precipitate with tannic acid, whilst nitrate of silver and protonitrate of mercury produce no change in it. The substance, dried at 266°, gave on analysis—

Carbon	74·08	20	= 1500	74·076
Hydrogen	7·44	12	150	7·405
Nitrogen	8·55	1	175	8·642
Oxygen	9·93	2	200	9·877

In the drying at 266° it loses 10·8 per cent. of water, which corresponds to 2 equivs.; so that the formula of the hydrated substance is that given above, whilst in the anhydrous state it is $C^{20}H^{12}NO^2$. This is precisely the composition of α-quinine.

Salts of β-quinine.—β-quinine forms, like α-quinine, basic and neutral salts, which have a very bitter taste. Some are more readily soluble than the corresponding salts of α-quinine, for instance, the oxalate, tartrate and acetate; on which account neutral oxalates, tartrates and acetates produce no precipitate in solutions of a salt of β-quinine, whilst a precipitate is formed in those of the corresponding salt of α-quinine. Some, on the other hand, are more insoluble; for instance, the muriate and nitrate of β-quinine.

Basic Muriate of β-quinine, $2\beta Ch + ClH + 2HO$, is easily procured by saturating the base with dilute muriatic acid. It crystallizes in very transparent white crystals, is soluble in alcohol and water, and differs from the corresponding muriate of quinine only by containing 1 equiv. less water. The air-dried salt lost at 248° 4·79 per cent. water. The air-dried salt furnished on analysis—

β-quinine	..	2	= 4050·0	85·2
Muriatic acid	9·48	1	455·5	9·9
Water	4·79	2	225·0	4·9

The corresponding salt of α-quinine contains 3 equivs. of water.

Chloroplatinate of β-quinine, $\beta Ch, HCl + PtCl^2 + 2HO$.—The preceding salt, dissolved in water with the assistance of a few drops of muriatic acid, furnishes, with an excess of neutral chloride of platinum, an orange-coloured precipitate, which, when washed and dried, appears to consist of 1 equiv. chloride of platinum, 1 equiv. muriate of β-quinine, and 2 equivs. water. The air-dried salt lost 4·86 per cent. of water at 212°. It has consequently the same composition as the corresponding double salt of α-quinine. The air-dried salt furnished on analysis—

Pt	26·25	1	= 1232	25·6
Cl	27·85	3	1333	27·6
HO	4·86	2	225	4·8
$\beta Ch + H$	42·55	1	2026	42·0

Neutral Muriate of β-quinine is obtained when dry muriatic gas is passed over β-quinine dried at 266°. It crystallizes from the solution in water, which was not found to be the case with α-quinine, which was treated in the same manner for comparison; this latter formed on evaporation a gelatinous mass. 100 parts of β-quinine, dried at 266°, absorbed 22·518 per cent. of muriatic acid gas; 100 parts of α-quinine, dried at 212°, absorbed 22·864 per cent.; the same quantity therefore. The calculated amount for these neutral salts is 22·4 per cent.

Basic Sulphate of β-quinine, $2\beta Ch + SO^3 + 6HO$.—Its preparation has already been described; it has a striking resemblance to the corresponding salt of α-quinine, but is more woolly and soft to the touch; it dissolves at 50° in 32 parts of absolute alcohol and in 350 parts of water, whilst the salt of α-quinine requires 740 parts of water at the same temperature. Moreover, the α-salt contains 7 equivs. of water.

The air-dried salt, heated to 266°, lost 12·838 per cent. of water. The air-dried salt furnished on analysis—

β-quinine		2 =	4050	77·5
Sulphuric acid	9·58	1	500	9·6
Water.....	12·84	6	675	12·9

Neutral Sulphate of β-quinine is readily obtained by adding a few drops of sulphuric acid to the solution of the preceding salt and evaporating. It crystallizes, but is very soluble in cold water.

Nitrate of β-quinine.—An excess of β-quinine is digested with dilute nitric acid, filtered and evaporated; it forms large crystals with a vitreous lustre. It differs from the corresponding α-quinine salt, as this does not crystallize under similar circumstances; it must be first evaporated to expel the excess of acid, and be then dissolved in water, when it is also obtained crystallized.

Oxalate of β-quinine, $\beta Ch, C^2 O^3 + HO$, cannot be obtained by precipitating a salt of β-quinine by an oxalate, as is the case with α-quinine, on account of its easy solubility. The base is therefore accurately saturated with the acid. From hot saturated solutions it separates on cooling in crystals with a nacreous lustre. The air-dried salt, when heated to 248°, lost 1·32 per cent. = 1 equiv. water. It has therefore the same composition as the corresponding salt of α-quinine. On analysis it furnished—

β-quinine..... ..		1 =	2025·0	78·3
Oxalic acid	16·58	1	450·0	17·4
Water	4·32	1	112·5	4·3

Tartrate of β-quinine is obtained with tartaric acid in the same manner as the preceding. It forms nacreous crystals.

Acetate of β-quinine is very easily soluble, and therefore difficult to obtain in crystals; if however its solution is evaporated to a syrupy consistence, some beautiful transparent crystals form in it in the course of a few days, which are distinguished in appearance from the nacreous crystals of the acetate of α-quinine.

From this similarity we may conclude that the β-quinine is like-

wise a febrifuge. Bauduin has found it to be quite as effective in cases of intermittent fever as α-quinine. Should this result be confirmed, the price of the preparations of quinine will be considerably reduced; for 100 parts of unadulterated quinoidine furnished—

3 per cent. of α-quinine,
From 6 to 8 per cent. cinchonine, and
From 50 to 60 per cent. β-quinine,

in an operation, which, executed upon a large scale, would furnish a still greater amount of produce. The preparation of β-quinine is likewise not very expensive.—*Scheikund. Onderzoech*, Part V. No. 4. p. 234.

Observations on the preceding Article.
By Dr. W. Knop.

Besides the results contained in the preceding abstract, the author gives in the introduction an historical view of all that had been previously published on the subject worth mentioning. After the discovery of quinine and cinchonine by Caventou in 1820, several chemists thought that a third uncrystallizable alkaloid occurred in the barks of the cinchonas. In 1820 Serturner described quinoidine, and ascribed to it a twenty times more powerful action against fever than to quinine. In 1830 Henry and Delondre decomposed quinoidine into quinine, cinchonine, a resin and an alkaloid, which they called quinidine. Guibourt, who examined it at about the same time, found no quinidine, but quinine, cinchonine and a yellow resin. Somewhat later Geiger showed that the quinidine of Henry and Delondre was crystallized hydrate of quinine, and that the quinoidine was a resinous substance which owed its antifebrile properties solely to the admixture of quinine and cinchonine. This was then generally admitted, even by Henry and Delondre, until Winckler, in 1843, asserted it to be amorphous quinine, combined with two not bitter resins, and contaminated with several other substances, as cinchonine, resins, &c., and described how it might be purified from them. Liebig, from analyses of purified quinoidine, arrived at the same view as Winckler, that quinoidine was amorphous quinine. Winckler subsequently announced that he had also detected amorphous cinchonine in it. Lastly, Roder published a paper, in which he asserted that, after separating the brown resin by means of protochloride of tin, the entire residue of quinoidine might be obtained crystallized, *i. e.* the amorphous quinine might be converted into crystalline, and obtained with a portion of crystallized cinchonine. Winckler could not succeed in confirming this statement.

Under such circumstances the question what is quinoidine would be difficult to answer; but if we consider the above facts after the admirable investigation of Van Heijningen, all these views are found to have some truth. Liebig's aim was to find a febrifuge which might be easily procured, so as to be applicable to poor practice. This gave rise to more rigid investigations; but even Heijningen's

results do not completely clear up the question. It is evident that quinoidine which has been purified from the brown extract, when the separation was very complete, the mere analysis must lead to the view of the existence of an amorphous quinine, since the results given by Heijningen exhibit a perfect agreement between the composition of the anhydrous α- and β-quinine; and that the cinchonine, the quantity of which is variable according to circumstances, may be present in so small quantity as to exert no evident influence upon the analysis. It is also evident that Roder's statement may be correct, since Heijningen shows that in this, as in many other well-known instances, the brown extract prevents the crystallization of the β-quinine. That Roder, being taken up with the amorphous quinine, did not distinguish the new base, is easily explicable, when we recollect that Heijningen says that the sulphate of the β-quinine has almost exactly the appearance of the sulphate of the α-quinine, which Roder considered to be the salt he obtained. As regards the immediate use of quinoidine as a therapeutic agent, in opposition to which both Mulder and Heijningen have written, the investigations of the latter show that the β-quinine constitutes a febrifuge which was unknown in the earlier investigations; and that when unadulterated quinoidine is given to the poor instead of the pure alkaloid, the proceeding has always the advantage of being less expensive. Nor can there be any objection to this, provided the brown extract is not injurious.—*Pharm. Cent. Blatt.*, July 11, 1849.

To preserve Milk or Cream.

To preserve milk or cream, according to Mr. Bethel, who has taken out a patent for this invention, it is first scalded, and then impregnated with carbonic acid gas in a soda-water machine. When the milk is charged with the gas, it is drawn off into bottles, and corked in the usual way; or, instead of being put into ordinary bottles (from which, as soon as opened, the whole quantity of milk must be poured out), it may be put into strong metal barrels, or cases, or jars, or bottles supplied with a cock or valve attached to a pipe leading to the bottom of the barrel, case, jar or bottle; so that, on opening the cock, a portion only of the milk may be drawn off at a time, the pressure of the gas within the barrel, case, jar or bottle being sufficient to force the milk out; and for keeping milk or cream a moderate time, it is sufficient to put the milk, after it has been scalded, into the metal barrels or vessels, and then force in the carbonic acid gas by an air-pump through the cock; or the milk or cream may be charged with carbonic acid gas by any other of the various means now well known for supplying carbonic acid gas to liquids. For milk or cream, the patentee prefers using carbonic acid gas made by the mixture of carbonate of soda and acid. The gas he washes in water before it is used, and he scalds or boils the milk before it is prepared.—Newton's *Journal*, August 1849.

PATENT.

Patent granted to Edward Schunck *for Improvements in the Manufacture of Malleable Iron.*

The first part of this invention relates to the manufacture of malleable iron from tin-plate scrap, which scrap consists of thin strips of plate iron, covered with tin, being the refuse and clippings obtained in the manufacture of articles from tin plate, or old articles of the same material, rendered useless by wear.

The presence of the tin has hitherto rendered tin-plate scrap unfit for the manufacture of iron; but by the present invention it is proposed to remove the whole of the tin from the surface of the plate before such is manufactured into malleable iron. By any one of the following processes the separation of the tin of the plate scrap from the plate iron may be effected:—

Process I.—The tinned plate scrap is placed in a boiling or hot solution of an alkaline sulphuret, containing an excess of sulphur; and of this class of substances the persulphuret of sodium is preferred, made either by dissolving sulphur in a solution of caustic soda, or by fusing sulphur with carbonate of soda, or by any other of the well-known methods of producing persulphuret of sodium. The excess of sulphur in this persulphuret changes the metallic tin into a sulphuret of tin; which sulphuret of tin is dissolved by means of the sulphuret of sodium (deprived of its excess of sulphur), forming a compound variously denominated by chemists as stannosulphuret of sodium and sulphostannate of sodium. By this process the iron is rendered perfectly free from the coating of tin.

Process II.—The tinned scrap is placed in a solution of oxide of lead in caustic potash or soda ley. During this process the tin becomes converted, by the action of the oxide of lead in the solution, into oxide of tin, which dissolves in the caustic potash or caustic soda, forming stannate of potash or stannate of soda; while metallic lead is precipitated from the solution in the form of a black powder. It is immaterial, as far as regards the ultimate effect, whether the solution of oxide of lead in caustic potash or soda ley be employed in a boiling state, or merely warm or cold; but the process goes on with much greater speed when the solution is employed at a temperature nearly approaching ebullition than when cold. By this process the iron is obtained nearly free from tin.

Process III.—The tinned scrap is placed in a solution containing a chromate of an alkali and caustic alkali, when the metallic tin becomes converted, by means of the chromic acid of the alkaline chromate, into oxide of tin, which dissolves in the excess of alkali, forming a stannate of the alkali, while chromic oxide is precipitated, and the iron is left nearly free from tin.

Of these processes the patentee prefers the first, in consequence of the inconvenience experienced from the precipitated metallic lead of the second process, and the precipitated chromic oxide of the third.

The iron, deprived of its coating of tin by either of the above processes, is washed well with water, in order to remove the excess of the solutions employed, which may adhere to it; and in case the second or third process is used, to remove the precipitated metallic lead or precipitated chromic oxide mechanically adhering to it. After allowing the liquor to drain, the pieces of scrap iron are packed closely in cylinders or pipes of sheet iron,—each pipe having a capacity of about one cubic foot, and being made to contain, by means of a slight degree of compression, about 80 lbs. weight of material. A pipe thus filled with scrap iron is placed in the fire, and when brought to a welding heat it is removed therefrom, and subjected to hammering in the way usually employed for making bar iron. This process of heating in the fire, and hammering while hot, is repeated until the whole mass becomes uniformly solid.

The second part of the invention relates to the recovery of the tin from the solutions employed for separating it from the iron, as described in the first part of the invention. The alkaline stanno-sulphuret obtained by the process first described is very soluble. This solution is boiled down in iron vessels until a drop crystallizes on cooling. The whole is then allowed to crystallize, and the crystals are drained on strainers made of iron-wire gauze. The crystals are next subjected to pressure, in order to squeeze out as much of the liquid which hangs about them as possible; after which they are placed in a reverberatory furnace, such as is generally used for the smelting of tin ores. By the application of a low heat in this furnace the crystals are completely dried and slowly roasted; by which means the sulphur of the sulphuret of tin is partly driven off and partly burnt, the sulphuret being changed thereby into oxide of tin. Then upon the roasted mass a mixture of small coal, charcoal, or any other carbonaceous substance, with dry carbonate of soda or quicklime, is thrown; and, the heat being raised in the furnace, the oxide of tin is reduced, and metallic tin obtained, which is run off through a hole at the bottom of the furnace. The slack which is left in the furnace is raked out; and, as it consists principally of alkaline sulphuret, it is dissolved in water; and, after an addition of fresh sulphur, it is suitable for being again used to strip fresh quantities of scrap iron of its metallic tin. The solutions of alkaline stannate obtained by the second and third processes are boiled down in iron vessels until crystals of the alkaline stannate are deposited; which crystals, as they form, are removed by means of an iron scoop, perforated with holes, and are placed as before on iron-wire gauze strainers to drain; the crystals are then pressed, and mixed while still moist with small coal, charcoal, or any other carbonaceous substance, and placed in a reverberatory furnace. By the application of heat, in the usual way, metallic tin is obtained, which is drawn off as before. The slack consists in this case principally of carbonate of soda, which is dissolved in water, and rendered caustic by means of quicklime; and by adding to it either oxide of lead or an alkaline chromate, a liquor is obtained suitable for stripping the tin from fresh quantities of tinned plate, as before.—Sealed Nov. 29, 1848.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Atomic Weights of Cerium, Lanthanium and Didymium. *By* C. Marignac.

In the first part of this memoir*, I stated that it was easier to obtain the oxide of cerium contained in the mixture of the oxides extracted from cerite in a state of purity, by treating it first with very dilute nitric acid, and then with a more concentrated acid, which deprives it of the last traces of lanthanium and didymium. By following an analogous process, the oxides of the two last metals are obtained free from cerium, by evaporating to dryness the solution effected by very dilute acid, calcining the residue, and digesting it afresh with nitric acid diluted with at least 200 times its weight of water; but the separation of these two oxides presents quite another difficulty. It is well known that the process discovered by M. Mosander to accomplish this separation is founded on the difference in solubility of the sulphates of these oxides at different temperatures. Both are very soluble in water at 41°–43° F., and are for the greater part precipitated by a higher temperature. But the sulphate of lanthanium is already precipitated from a concentrated solution at a temperature below 86°, whilst the sulphate of didymium still remains almost entirely in the liquid, and is only separated at a higher temperature. This property allows of obtaining at last perfectly pure sulphate of lanthanium, provided that a sufficient quantity of salt is operated upon to be able to repeat this operation a considerable number of times.

It is necessary, therefore, after having converted the oxides into sulphates, to calcine the latter at a dull red heat in order to render them anhydrous, to pulverize them, then to convey them gradually into from 5 to 6 times their weight of water, taking care to agitate the liquid continually, and to keep it immersed in water at 32°, in order to avoid the considerable elevation of temperature, which would otherwise result from the hydration of the sulphates. The solution is then filtered, and kept for several hours at a temperature between 86° and 95°. The sulphate of lanthanium is precipitated in minute colourless crystals, and the solution has a rose

* Page 212 of the present volume.

colour from the sulphate of didymium. The liquid is decanted, the crystals washed on a funnel with a little water, then calcined, and the operation repeated. It will be understood that in each operation some sulphate of lanthanium remains in the liquid and in the wash-water, so that the weight of the product rapidly diminishes in proportion as its purity increases. The first crops of crystals of the sulphate of lanthanium, when viewed in mass, still exhibit a faint rosy tint; the subsequent crops appear colourless; but if the solution from which the salt has crystallized is evaporated to dryness, the residue is rose-coloured, indicating that there was still a little sulphate of didymium present. Now this treatment must be continued until the residue left on evaporation is itself perfectly colourless. I think, when this has been attained, we may be certain of the purity of the sulphate of lanthanium; at least I have found that the salt now deposited by the first elevation of temperature and that obtained on evaporation to dryness have exactly the same appearance and furnish the same equivalent.

Thus the purification of the sulphate of lanthanium may be accurately attained by this process; it merely requires patience and a sufficient quantity of material. Unfortunately this is not the case with the sulphate of didymium, which is left in the solutions mixed with sulphate of lanthanium. When these solutions are submitted to a slow evaporation between 104° and 122°, they deposit pretty large crystals of sulphate of didymium, of a bright rose colour, mixed with a large quantity of minute crystals of a lighter rose-colour, and which are probably more contaminated with lanthanium. Now the most perfect crystals in form and colour should be carefully selected, and this separation by crystallization several times repeated; in this operation patience and a quantity of material are indispensable. In each operation a purer product is obtained, but we have no means of ascertaining its purity.

I have unsuccessfully attempted the use of a number of reagents, trying their action on the mixed oxides, or by causing them to act separately on each of the two oxides. I have not been able to discover the least difference which might lead to the detection of a more accurate process of separation, or even quicker than that above described, and which is nothing more than Mosander's.

I will nevertheless mention two processes, which, without leading even to an approximative separation of these two oxides, appear to me capable of being usefully applied in the treatment of their mixture, when they are in such relative proportions that the crystallization of the sulphates no longer furnishes any result.

If these sulphates are converted into oxides, either by precipitating them at different intervals by carbonate of soda at a boiling temperature or in any other manner, and if, after having strongly calcined these oxides, they are left in contact for a very long time at the ordinary temperature with a very large amount of water containing nitric acid, but not in sufficient quantity to dissolve the whole, a very slightly coloured solution is obtained rich in oxide of lanthanium; whilst the residue, dissolved in its turn in nitric acid,

furnishes a more highly coloured solution, and which is consequently richer in didymium.

Another process is founded on a slight difference of solubility of the oxalates. Both are very insoluble in water, and very sparingly soluble in dilute acids, so that these oxides may be almost entirely precipitated by oxalic acid from their neutral sulphuric and muriatic solutions. If the oxalates thus precipitated are heated with a large quantity of muriatic acid diluted with its volume of water, they are completely dissolved, and are subsequently precipitated by the evaporation of the liquid; but we then observe that the first precipitates are more rose-coloured than the last, so that we may by this means obtain a mixture containing more oxide of didymium, and another mixture containing more oxide of lanthanium.

These two processes, it will be seen, do not effect even an approximate separation. I employed them merely to obtain a mixture rich in didymium, capable of being purified by conversion into sulphate and crystallization.

Pure sulphate of lanthanium is perfectly colourless; it most frequently crystallizes in small, slender and very short acicular prisms. It may however be obtained in determinable crystals, although very small, by spontaneous evaporation; they are hexahedral prisms terminated by a six-sided pyramid, like quartz. The minuteness of the crystals renders the measurements difficult; however, all my observations agree in proving the angle of the prism not to be 120°, but only 119° 30′; the primitive form therefore is a right rhombic prism. This salt contains 3 equivs. of water of crystallization, like the sulphate of cerium.

The sulphate of didymium is of a somewhat deep and pure rose colour; it crystallizes readily in very brilliant and sometimes tolerably large crystals, which belong to the oblique rhombic prism. The crystals are frequently mackled parallel with the anterior angle of the prism; they are easily cleavable in the direction of the base. The faces of the primitive rhomboidal prism are not met with; but a large number of modifications are observed, among which I shall especially mention the oblique rhomboidal octahedron (d^1, b^1), and the usual truncations on its front edge (o^2) and on its posterior one (a^2). The following are the principal angles:—

		°	′
Inclination of the axes P on h^1		118	8
Angles of the octahedron	on the front edge d^1 on d^1	78	48
	on the posterior edge b^1 on b^1	54	12
	on the lateral edge b^1 on d^1	143	49
Inclinations of the base P	on the faces d^1	125	20
	on the faces b^1	110	3
	on the face o^2	155	40
	on the base a^2	138	49

This salt likewise contains 3 equivs. of water of crystallization. It is remarkable that the sulphates of these three oxides, notwithstanding the great analogy which they exhibit in all their properties

and their containing the same proportion of water of crystallization, are nevertheless not isomorphous. Those of cerium and lanthanium, it is true, belong to the same system, that of the right rhomboidal prism; but their angles do not allow of their being connected one with the other.

I shall now proceed to the determination of the equivalents of the salts.

Atomic Weight of Lanthanium.—I first followed, for the analysis of the sulphate of lanthanium, the method which I have described for that of the sulphate of cerium, which is based upon the mutual precipitation of this salt and the chloride of barium and on the employment of normal solutions. The same difficulties occur as with the sulphate of lanthanium; an inspection of the results obtained appears even to indicate in the present case greater uncertainty; not only is there frequently a much greater difference between the two limits which should comprise the true equivalent, but I have not obtained perfectly constant results in several successive experiments, even on operating on the product of one and the same preparation. The following however are the results:—

	Sulphate of lanthanium.	Chloride of barium.		Equiv. of sulphate of lanthanium.		
		Minimum.	Maximum.	Maximum.	Minimum.	Mean.
1.	11·644	12·765	12·825	1185·8	1180·3	1183·0
2.	12·035	13·195	13·265	1185·7	1179·4	1182·5
3.	10·690	11·669	11·749	1190·9	1182·8	1186·8
4.	12·750	13·920	14·000	1190·7	1183·9	1187·3
5.	10·757	11·734	11·814	1191·8	1183·7	1188·7
6.	12·672	13·813	13·895	1192·6	1185·8	1189·2
7.	9·246	10·080	10·160	1192·4	1184·3	1188·3
8.	10·292	11·204	11·264	1194·2	1187·8	1191·0
9.	10·192	11·111	11·171	1192·5	1186·1	1189·3

It is evident that some of the results differ too much from the mean to be free from error, and it is advisable in calculating this mean to omit the experiments 1, 2 and 8; we then obtain the number 1188·3. I have endeavoured to check this result by following a slightly different process, which appears to me to be applicable under various circumstances.

I accurately dried and weighed off very nearly equivalent quantities of sulphate of lanthanium and chloride of barium, taking care to have a slight excess of the latter; I then used a solution of the chloride to precipitate the acid of the first salt, following in every respect the ordinary rules for estimating sulphuric acid, only that I subsequently mixed the filtered liquid and the whole of the wash-water, and evaporated it down to a very small bulk; and then, by adding a few drops of sulphuric acid, precipitated the baryta which had remained in excess in the decomposition of the two salts. The sulphate of baryta obtained in this second operation was collected, washed with care and dried. Knowing the weight of the chloride of barium employed, the quantity of sulphate of baryta corresponding

to it can be calculated; and if we deduct from it the weight of the sulphate obtained in the second precipitation, the difference expresses the weight of that which ought to have been precipitated by the mixture of the two saline solutions. If we compare this weight with that furnished by direct experiment, the latter is always found to be too high however long the washing may have continued; and it is easily ascertained that this mass of sulphate of baryta contains a notable quantity of lanthanium, by treating it after calcination with hydrochloric acid. It will be understood that the error resulting from this mixture should be at least proportional to the weight of the sulphate of baryta obtained; and that consequently this error is diminished at will by making the weight of the total mass of this sulphate depend on that of the slight precipitate obtained in ascertaining the excess of baryta left in the filtered liquids and the wash-waters of the first precipitate. Two experiments made according to this method gave—

Sulphate of lanthanium.	Chloride of barium.	Sulphate of baryta.			Equiv. of the sulphate of lanthanium.
		1st precip.	2nd precip.	Calculated.	
4·346	4·758	5·364	0·115	5·329	1187·4
4·733	5·178	5·848	0·147	5·803	1188·3

By combining these results with those obtained by the other method, and with which they agree very well, we find that the number 588 may be admitted to represent very approximately the equivalent of lanthanium.

The determinations hitherto made of this equivalent exhibit great variations; thus

M. Choubine has adopted the number			451·88
M. Rammelsberg	...	...	554·88
M. Mosander	...	...	580
M. Hermann	...	...	600

My results come very near to those of M. Mosander. M. Hermann, denying the existence of didymium, did not separate it from lanthanium, which must have raised its atomic weight beyond the true number.

Atomic Weight of Didymium.—As stated above, I have not been able to find any means of detecting the presence or absence of lanthanium in the sulphate of didymium, I shall therefore confine myself to enumerating the results of the determinations of the equivalent of this salt made upon several samples obtained after repeated crystallization. They were made according to the method last described:—

Sulphate of didymium.	Chloride of barium.	Sulphate of baryta.			Equiv. of sulphate of didymium.
		1st precip.	2nd precip.	Calculated.	
3·633	3·902	4·412	0·084	4·373	1210·4
3·862	4·227	4·679	0·075	4·662	1206·9
3·330	3·552	4·027	0·088	3·980	1218·7
1·386	1·477	1·681	0·014	1·655	1219·9

As it cannot be expected that the last traces of lanthanium have been removed by crystallization, and that the presence of this metal must diminish the equivalent of the didymium, the preceding numbers can merely indicate a lower limit of this equivalent, and the last results, the highest, must be the nearest to truth; we may thence conclude that the equivalent of didymium is at least equal to 620, perhaps higher; at all events it is not probable that it exceeds much this figure.—*Bibliothèque Univers. de Genève*, May 1849.

On the Products of Oxidation of the Volatile Distillates of the Fats. *By* F. C. Schneider.

At present we are acquainted with several modes in which the volatile fatty acids are produced. They are formed by the saponification of fats, by putrefaction, distillation and oxidation of more highly compound fatty acids, especially from oleic acid, hydrocarbons and proteine compounds. In all these modes of formation, a very complex atom is decomposed into a simpler one, generally with the simultaneous assimilation of oxygen. Oleic acid behaves in this respect very characteristically. If oxygen is conveyed to it by means of nitric acid, a whole series of volatile fatty acids is produced; if it be submitted to destructive distillation, it furnishes principally hydrocarbons, along with small quantities of fatty acids. The author put the question, whether the hydrocarbons separated in this operation, consequently after they had been eliminated from the composition of oleic acid, might still be converted into the same volatile acids by oxidizing agents.

The result of this investigation is, that these hydrocarbons can certainly be converted into fatty acids by oxidizing agents, such as the alkalies, nitric and chromic acid; but all the oxidizing agents have not an equally favourable action. Nitric acid is the best, which furnishes the greater number of the volatile acids from acetic acid to caprylic acid inclusively. The reason of this is owing to the circumstance, that this acid produces at the same time a nitro-compound, which consists of a mixture of hyponitric acid and a volatile oil with a greater amount of oxygen than is contained in the original hydrocarbon, and of fatty acids. This compound prevents the higher fatty acids which principally occur in it, for instance the caprylic acid, which could only be detected in the nitro-substance, from further oxidation. Chromic acid, on the contrary, furnishes only the volatile acids of the most simple constitution; because, in the absence of a similar collateral product which might resist its ulterior action, the more complex acids are further decomposed.

Among the products of distillation of the fatty oils, and of those fatty acids which are either not volatile, like the oleic and stearic acids, or whose point of decomposition is situated very near their boiling-point, other acids, and also acroleine, occur with the hydrocarbons. The hydrocarbons must therefore be first freed from the latter substances; for which purpose the retort is connected with

several Wolf's bottles, in which the less volatile products of distillation separate from those which are more readily volatile.

The hydrocarbons which served for this investigation were prepared by distilling rape-oil; they were then left for a long time in contact with oxide of silver to remove the acroleine and the acids contained in them, then distilled with water, and lastly rectified alone. The liquid thus obtained, dried over chloride of calcium, is a mixture of hydrocarbons in which carbon and hydrogen are contained in the atomic proportion of $C^6 : H^5$. It is colourless and of a penetrating odour, resembling acroleine. In the air, and after long standing even in closed vessels, it becomes yellow. It has no action upon vegetable colours; but when dissolved in alcohol, it reddens after a time blue litmus-paper which has been moistened with it. The boiling-point rises uninterruptedly from 162° to 347°. Analysis gave—

Carbon	86·19	86·39	86·17
Hydrogen	12·15	11·96	11·97
Oxygen	1·66	1·65	1·86

The vapours of these hydrocarbons distil over moderately heated soda-lime with scarcely any alteration; but if the temperature is higher, the soda-lime is coloured brown by separated carbon, the disagreeable odour of the hydrocarbons is converted into one which is less so, and very little passes over unaltered. On decomposing the soda-lime with sulphuric acid, carbonic acid is disengaged in both cases, and in the residual liquid butyric and valerianic acids are detected.

Treatment of the Hydrocarbons with Nitric Acid.—The mixture of hydrocarbons was treated with nitric acid in a retort the neck of which had an upward direction, which was lengthened by an accurately-fitting well-cooled glass tube, in order that the ascending vapours might be condensed and flow back. As soon as small quantities of the hydrocarbons come into contact with concentrated nitric acid, the mass becomes heated, red vapours of nitrous acid are given off, and a cinnamon-like odour, as well as one of prussic acid and oil of bitter almonds, is perceptible; the liquid is dark-coloured, and a resinous viscid mass separates on the sides of the vessel. When the oxidation is continued by fresh additions of nitric acid, this resinous mass gradually disappears, and the contents of the retort become homogeneous. As soon as the nitric acid has no further action even at a boiling temperature, the oxidation is complete, the evolution of red vapours ceases, and the liquid assumes a lighter colour; after long standing, especially in the cold, the liquid separates into two layers, the upper one of which is oily and of a dark colour, the lower one aqueous and lighter. Upon the addition of water, a brownish-red mass, I., of oily consistence, strong smell of oil of bitter almonds and acid reaction, separates, after long standing, at the bottom of the vessel. The turbid aqueous liquid, II., decanted from it, smelt of valerianic and butyric acids.

This aqueous liquid, II., was saturated with carbonate of potash

and evaporated. The crystals of nitre were separated from the mother-ley, and the latter decomposed with sulphuric acid, when an acid layer of fat separated on the surface. This layer of oil was separated from the liquid, saturated with barytic water, boiled, filtered boiling hot, the excess of baryta in the filtered solution precipitated by carbonic acid, again boiled, filtered, and the solution evaporated to crystallization. The crystals were acetate of soda. They were separated from the mother-ley, again dissolved, and their solution, as well as the mother-ley, each separately precipitated with nitrate of silver, in order to examine the silver salts of the acids present. The liquid separated from the layer of oil was distilled with water until what passed over no longer exhibited any acid reaction; it was then saturated with soda, and evaporated to crystallization. The crystals obtained were acetate of soda.

The Barytic Salts of the aqueous liquid, II., from which the excess of baryta had been removed by carbonic acid, are still contaminated with a substance containing hyponitric acid, the chief amount of which is contained in the heavy oily mass I. separated by water. Their solution is coloured yellow by it. On further treatment they were separated into the following salts:—

Œnanthylate of Baryta.—The solution deposits after evaporation yellow laminar crystals, which are obtained pure by repeated crystallization from the boiling-hot solution. On boiling, a resinous viscid mass separates, which is very insoluble in water. The purified crystals furnished on analysis—

	Found.			Calculated.
Atomic weight.....	195·30	194·30	194·50	197·64
Per-centage of baryta ..	39·24	39·43	39·38	38·78

Caproate of Baryta.—The mother-ley from the preceding crystals furnished on further evaporation warty groups of yellow needles, which were purified in the same manner as the œnanthylate of baryta. Analysis furnished—

	Found.			Calculated.
Atomic weight.....	183·30	183·30	184·00	183·60
Per-centage of baryta ..	41·80	41·82	41·53	41·73

Valerianate of Baryta.—The very thick mother-ley from the preceding salt deposited, after long standing, some shining laminæ, which, purified as above, consisted of valerianate of baryta. Analysis gave—

	Found.	Calculated.
Atomic weight	171·00	169·64
Per-centage of baryta	44·68	45·18

The remainder of the liquid does not crystallize, but dries to a gummy mass; it contains the lower fatty acids; a few granules of butyrate of baryta were perceptible in it. A more complete separation of the saline mass can be attained with nitrate of silver.

The separation of these salts of baryta is likewise rendered very difficult by the substance containing hyponitric acid, which is

equally combined with baryta, as it separates in the resinous tenacious state partly on the surface, partly on the sides of the vessel. The films which form on the surface must be removed and repeatedly exhausted with boiling water, when the mixture is decomposed, and furnishes a considerable quantity of fatty acids.

The Silver Salts of the aqueous liquid II., which were obtained after the separation of the acetate of soda by crystallization from the solution and the separated mother-ley, were found to consist of—

Acetate of Silver.—The silver salt prepared from the crystallized soda salt, which was instantly recognised to be acetate, possessed all the properties of the acetate of silver:—

	Found.		Calculated.
Atomic weight	166·70	167·00	167·00
Per-centage of silver	69·58	69·45	69·46

Valerianate of Silver separated on the cooling of the hot solution of the silver salt obtained from the mother-ley in white laminæ, which became black by exposure to the light. When purified, it furnished—

	Found.	Calculated.
Atomic weight	207·00	209·00
Per-centage of silver	56·29	55·50

Butyrate of Silver, crystallized from the liquid, separated from the preceding salt, on further evaporation and cooling, in dendritic crystals. It gave—

	Found.			Calculated.
Atomic weight.....	196·00	194·00	194·60	195·00
Per-centage of silver ..	59·11	59·70	59·31	59·48

Metacetonate of Silver separated on further evaporating the remaining liquid in minute hard granules, which became black on boiling, and melted quietly when heated; and indeed exhibited all the properties of the metacetonate of silver. A determination of the atomic weight furnished—

	Found.		Calculated.
Atomic weight	180·80	181·00	181·00
Per-centage of silver	64·16	64·07	64·09

An elementary analysis was made of the same salt, the results of which fully confirmed the above:—

Carbon.....	19·73	6	= 36	19·89
Hydrogen.....	2·67	5	5	2·76
Oxygen.....	13·64	3	24	13·26
Oxide of silver	64·16	1	116	64·09
	100·00		181	100·00

Metacetonacetate of Silver.—As soon as no more crystals of the metacetonate of silver separated, the mother-ley was further evaporated, when some shining dendritic crystals were obtained, which on

ignition left a delicate network of metallic silver. A determination of the atomic weight gave—

	Found.			Calculated.
Atomic weight.....	173·00	174·00	174·00	174·00
Per-centage of oxide of silver	66·74	66·55	66·45	66·59

Elementary analysis furnished—

Carbon.....	16·80	5	= 30	17·24
Hydrogen.....	2·41	4	4	2·29
Oxygen.....	14·13	3	24	13·88
Oxide of silver.....	66·66	1	116	66·59
	100·00		174	

In the residual mother-ley acetate of silver could be detected.

The Nitrogenous Compound, or the above-mentioned substance I. containing hyponitric acid, in the state in which it is precipitated by water, is oily, of a brownish-red colour, heavier than water, and has an acid reaction. When heated, it gives off red vapours at a temperature a little above that of boiling water, and becomes black by partial decomposition and separation of carbon. Fatty acids may be extracted from the blackened mass by means of potash. When the nitrogenous compound is distilled quickly after the addition of water, fatty acids are likewise obtained; but at the same time a portion of the oil is carried over into the receiver. It combines with bases, but does not furnish very characteristic salts; with potash, it gives an uncrystallizable compound of a dark brown colour; with baryta, a mass which cakes together; with oxide of silver, a fawn-coloured precipitate. When melted with hydrate of potash, the mass becomes brown, ammonia escapes, and the potash combines with fatty acids. Upon the addition of sulphuric acid, prussic acid is disengaged; and on distilling the liquid, a mixture of œnanthylic, caproic and valerianic acids is obtained, which are separated by forming their baryta salts.

The decomposition of the nitrogenous compound is best effected by passing into it a current of dry ammoniacal gas. A bright red liquid is formed, from which a heavy layer of oil subsides, which is neutral and not volatile, and most closely resembles in odour and colour the hydruret of benzoyle. It does not however furnish any benzoate of potash when mixed with an alcoholic solution of potash; but remains dissolved in it, and can again be precipitated by the addition of water. When the mixture is distilled, the alcohol passes over with an oil which has but a faint odour of oil of bitter almonds. This oil is scarcely soluble in water, and sinks in it. When rectified, an oily substance is again obtained, but some carbon is left in the retort; this separation of carbon takes place even after a second and third rectification. The rectified oil, on the other hand, has absorbed hydrogen and oxygen in the proportion to form water, as was ascertained by the elementary analysis of the two oils. When the alcohol is removed, more of the oily substance is obtained; and it can be entirely separated from the potash by continued distillation with

water. The oil was deprived of water by distillation over caustic lime. If, after removing the oil, the potash solution is decomposed with sulphuric acid and the mixture distilled, an acid liquid of a most disagreeable odour is obtained, which on saturation with baryta water furnished so small a quantity of salt, that the acid which it contained could not be determined.

The ammoniacal ley separated from the oily substance just described furnishes a copious precipitate with nitrate of silver after expelling the excess of ammonia. The greater portion of it dissolved in boiling water without becoming black, and again separated on cooling in white flakes. The portion which was not dissolved by the water dissolved in boiling alcohol, from which, on cooling and evaporating the alcohol, it separated as a white powder. It is caprylate of silver. The silver salt which separated from the aqueous solution was œnanthylate of silver. The succeeding crop of crystals proved to be a double compound of caproate and œnanthylate of silver.

Lastly, the mother-ley, when it appeared to be of constant composition, still contained silver salts of the next following lower fatty acids down to metacetonic acid.

The results which followed from the investigation of the products of oxidation of the more volatile hydrocarbons were again obtained in the examination of the same products from the less volatile hydrocarbons; but in the latter case the nitrogenous compound had the consistence of a salve; and the separation of the salts of baryta was rendered more difficult by the admixture of a larger amount of the resinous substance.

Treatment of the Hydrocarbons with Chromic Acid.—A mixture of bichromate of potash and sulphuric acid has a very feeble action upon the hydrocarbons at the ordinary temperature. On the application of heat, a very violent reaction occurs, and the greater part of the hydrocarbons distil over, which renders the operation very tedious. When all reaction has ceased, the mixture is distilled, the product saturated with soda, precipitated with nitrate of silver, and the silver salts separated. Only metacetonic and acetic acids could be detected; the latter in greatest abundance.—Liebig's *Annalen*, lxx. p. 107.

On Laurent's and Gerhardt's Equivalents and Notation.
By Ch. Gerhardt.

I shall give in the following the principal features of the mode of notation adopted by Laurent and myself. Our method appears to us to be at the same time more accurate and more simple than the dualistic method. The numerical value of our symbols is, with respect to the metalloids, the same as in Berzelius's mode of notation; but for the *metals** it amounts to only the half; we write

* Except arsenic, antimony, bismuth and uranium, which have the same value as with Berzelius.

HO, SO^2, SO^3, PO^5, CO, CO^2, &c. Even HCl, HBr and NH^3 have the same value; but in the metallic compounds the symbol of the metal is only the half of Berzelius's number:—

Examples.	Berzelius's notation.	Our notation.
Sulphuretted hydrogen	H^2S	$S(H^2)$
Sulphuret of potassium	KS	$S(K^2)$
Hydrochloric acid	H^2Cl	Cl(H)
Chloride of potassium.....	KCl	Cl(K)
Sulphuric acid.....	SO^3, H^2O	$SO^4(H^2)$
Sulphate of potash	SO^3, KO	$SO^4(K^2)$
Bisulphate of potash	$SO^3, KO + SO^3, HO$	SO^4, HK
Sulphate of zinc and potash ..	$SO^3, KO + SO^3, ZnO$	$SO^4(ZnK)$
Nitric acid	N^2O^5, H^2O	$NO^3(H)$
Nitrate of potash.....	N^2O^5, KO	$NO^3(K)$

The chief difference consists therefore in the way of writing the salts which we regard as units, in which one metal may be substituted for another without the molecular system being altered. In general we place the metal in parentheses. According to this view the true acids (the hydrates of the oxyacids and the hydracids) are salts in which the metal is represented by hydrogen; the oxides, sulphurets, &c. have the same right to the name of salt as the sulphates and nitrates. The so-called anhydrous acids we view as peculiar substances, which become acids only by the fixation of the elements of water.

We further assume, *that one and the same body may have one or several equivalents.* It is well known that one element frequently plays the part of two or several other very different elements, whence it may arise that each of these different functions is likewise represented by different quantities of the first element. On the other hand, it is sometimes seen that different quantities of a metal, for instance, of iron, copper, mercury, replace the hydrogen of acids, and form salts which contain the same metal but exhibit different properties. According to our view, therefore, the metals have likewise different equivalents. A few examples will render this essential point of our doctrine more intelligible.

First Example.—The sulphate of the protoxide of iron and the sulphate of the peroxide of iron are two salts which for the same quantities of sulphur and oxygen contain different quantities of iron. If we express by S=16 the amount of sulphur, by O=8 the amount of oxygen, and by Fe=28 the amount of iron, we have—

Sulphate of the protoxide of iron, $SO^4Fe = SO^3, FeO$
Sulphate of the peroxide of iron, $SO^4Fe\frac{2}{3} = 3SO^3, Fe^2O^3$ } according to Berzelius.

In the sulphate of the peroxide of iron there is only $\frac{2}{3}$rds of the quantity of iron contained in the sulphate of the protoxide of iron; but these $\frac{2}{3}$rds of the iron are equivalent to the H, K, Na, Zn, &c., just as much as the Fe in the protosalts of iron. Now since $\frac{2}{3}$Fe replace H in sulphuric acid or K in the sulphate of potash, we obtain a salt which, although a neutral salt, differs by its properties from the sulphate of the protoxide of iron, in which one Fe entirely

replaces H, K, Na, Zn. The equivalent $Fe\frac{2}{3}$ consequently imparts to sulphuric acid properties which are as different from those of the sulphate of the protoxide of iron as from those of any other sulphate containing a different metal.

Second Example.—In the protochloride of mercury and in the perchloride of mercury the same amount of chlorine is combined with different quantities of mercury:—

Protochloride of mercury .. Hg^2Cl^2
Perchloride of mercury .... $HgCl^2$ } according to Berzelius.

But, in the salts of the protoxide of mercury, Hg^2 is the equivalent of H, K, Na, Pb, &c., just as much as Hg in the persalts. Mercury has, therefore, according to our theory, with reference to other metals, 2 equivalents (mercuricum and mercurosum), which are to each other as 1 to 2, and which both possess different properties.

In order to show that in the formulæ $Fe\frac{2}{3}$, Hg^2, &c., express equivalents of H, K, Na, &c., we frequently replace the coefficients by peculiar signs; we employ for this purpose the Greek letters $\alpha, \beta, \gamma, \delta$, instead of the numbers 2, $\frac{2}{3}$, $\frac{1}{2}$, $\frac{1}{3}$, &c.

The following are equivalent to water in the following salts:—

$2=\alpha$

Cu in the salts of the peroxide of copper. Cu^2 or $Cu\alpha$ in the protosalts of copper.

Hg in the persalts of mercury. Hg^2 or $Hg\alpha$ in the protosalts of mercury.

$\frac{2}{3}=\beta$

Fe in the protosalts of iron. $Fe\frac{2}{3}$ or $Fe\beta$ in the persalts of iron.

$Al\frac{2}{3}$ or $Al\beta$ in the salts of alumina.

Cr in the salts of the protoxide of chromium. $Cr\frac{2}{3}$ or $Cr\beta$ in the persalts of chromium.

Mn in the protosalts of manganese. $Mn\frac{2}{3}$ or $Mn\beta$ in the persalts of manganese.

$\frac{1}{2}=\gamma$

Sn in the protosalts of tin. $Sn\frac{1}{2}$ or $Sn\gamma$ in the persalts of tin.

Pt in the protosalts of platinum. $Pt\frac{1}{2}$ or $Pt\gamma$ in the persalts of platinum.

$\frac{1}{3}=\delta$

$Bi\frac{1}{3}$ or $Bi\delta$ in the salts of bismuth.
$Sb\frac{1}{3}$ or $Sb\delta$ in the salts of the oxide of antimony.
$Au\frac{1}{3}$ or $Au\delta$ in the salts of the oxide of gold.

The following salts are written—

According to Berzelius.	According to our notation.
Alum	
$SO^3, KO + Al^2O^3, 3SO^3 + 24Aq.$	$SO^4(K\frac{1}{2}Al\beta\frac{1}{2}) + 6Aq.$
Sulphate of Potash	
SO^3, KO	$SO^4(K^2).$

According to Berzelius.	According to our notation.
Phosphate of Soda	
$P^2O^5, 2NaO, H^2O + 24Aq.$	$PO^4(NaH) + 12Aq.$
Biphosphate of Soda	
$P^2O^5, NaO, 2HO + 2Aq.$	$PO^4(NaH) + Aq.$
Phosphate of Lead	
$P^2O^5, 3PbO.$	$PO^4(Pb^3).$
Phosphate of Alumina	
$3P^2O^5, Al^2O^3.$	$PO^4(Al\beta^3).$

The simplicity of our mode of notation is especially evident in those salts which contain several metals, as the native silicates. For instance, the formula of chlorite from Slatoust is, according to Berzelius—

$$3MgO, SiO^3 + Al^2O^3, SiO^3 + 2(MgO, 4H^2O).$$

We write it—

$$SiO^3(Al\beta\tfrac{3}{5}Mg\tfrac{4}{5}H\tfrac{1}{5}).$$

This formula at the same time shows that chlorite belongs to the silicates* of the formula

$$SiO^3(M^4)$$

for $\frac{3}{5}+\frac{4}{5}+\frac{1}{5}=4$.

The advantage of our method consists therefore principally in this, that all salts of the same genus can be expressed in the same manner. Each symbol occurs only once in one formula. *We therefore write similar compounds in the same manner.*

In representing organic substances, we take the volumes into consideration in the case of substances which may be volatilized without decomposition; we denote the latter by the same number of volumes, and the definite compounds derived from them by similar formulæ. Thus we represent the monobasic acids by that quantity which contains 1 equiv. of basic H; it corresponds to 2 vols. of vapour. Those derived substances which do not behave like salts are expressed by the same number of volumes; if these derivatives are not volatile, we assume that quantity as the equivalent which is yielded by 1 equiv. of the monobasic acid, or which furnishes 1 equiv. of this acid:—

Examples.	According to Berzelius.	According to our method.
Acetic acid	$C^4H^6O^3, H^2O$	$C^2H^3O^2(H)$
Acetate of potash	$C^4H^6O^3, KO$	$C^2H^3O^2(K)$
Peracetate of iron	$3C^4H^6O^3, Fe^2O^3$	$C^2H^3O^2(Fe\beta)$
Chloroacetic acid	C^2O^3, C^2Cl^6, H^2O	$C^2Cl^3O^2(H)$
Chloroacetate of potash	C^2O^3, C^2Cl^6, KO	$C^2Cl^3O^2(K)$
Chloroacetate of the peroxide of iron	$3(C^2O^3, C^2Cl^6), Fe^2O^3$	$C^2Cl^3O^2(Fe\beta)$
Alcohol	C^2H^6O	C^2H^6O
Aldehyde	$C^4H^8O^2$	C^2H^4O
Olefiant gas	CH^2	C^2H^4.

The bibasic acids are not volatile without decomposition; consequently the general rule with regard to the volumes does not apply

* Silica = SiO.

to them; however, these acids furnish volatile anhydrides on their decomposition. We therefore assume as the formula that quantity which furnishes 2 vols. of anhydride; the bibasic acids are therefore denoted by basic H^2:—

Examples.	According to Berzelius.	According to our method.
Oxalic acid	C^2O^3, H^2O	$C^2O^4(H^2)$.
Oxalate of potash	C^2O^3, KO	$C^2O^4(K^2)$
Binoxalate of potash ..	$C^2O^3, KO + C^2O^3, H^2O$	$C^2O^4(HK)$
Tetroxalate of potash ..	$C^2O^3, KO + 3(C^2O^3, H^2O)$	$C^2O^4(H\frac{1}{2}K\frac{1}{2})$.

In the same manner the tribasic acids are designated by basic H^3:—

Examples.	According to Berzelius.	According to our system.
Citric acid.....	$3C^4H^4O^4, 2HO$	$C^6H^5O^7(H^3)$
Acid citrate of potash	$3C^4H^4O^4, KO, HO$	$C^6H^5O^7(KH^3)$
Another citrate of potash..	$3C^4H^4O^4, 2KO$	$C^6H^5O^7(K^2H)$
Third citrate of potash....	$C^{12}H^{10}O^{11}, 3KO$	$C^6H^5O^7(K^3)$.

For the sake of analogy, we characterize the mineral acids with H, H^2, H^3, according as they are mono-, bi- or tri-basic.

Most chemists express organic substances by formulæ which are double of ours; but all these formulæ, when they are correct, may be divided by two, and represented according to our method.

In conclusion, I have added a table of the equivalents of the principal simple bodies:—

		H=1.	O=100.			H=1.	O=100.
H	Hydrogen ..	1	6·25	Cl	Chlorine....	35·5	221·87
Li	Lithium	6·4	40·16	K	Potassium ..	39	243·75
B	Boron.....	10·8	67·50	Sr	Strontium ..	44	275·00
C	Carbon	12	75·00	Cd	Cadmium ..	56	350·00
Mg	Magnesium	12	75·00	Sn	Tin.....	59	368·75
Al	Aluminium..	13·7	85·63	Sb	Antimony ..	64·5	403·25
N	Nitrogen ..	14	87·50	Ba	Barium	68	425·00
Si	Silicon	14	87·50	As	Arsenic	75	468·50
O	Oxygen	16	100·00	Se	Selenium ..	78·5	490·90
Fl	Fluorine....	18·6	116·85	Br	Bromine....	80	500·00
Ca	Calcium	20	125·00	W	Tungsten ..	96	600·00
Na	Sodium	23	143·75	Pt	Platinum ..	99	618·75
Cr	Chromium ..	26	162·50	Hg	Mercury....	100	625·00
Fe	Iron	28	175·00	Pb	Lead	104	650·00
Mn	Manganese..	28	175·00	Ag	Silver.....	108	675·00
Ni	Nickel	29·6	185·00	U	Uranium ..	120	750·00
Co	Cobalt	29·6	185·00	J	Iodine.....	126	787·50
Cu	Copper	31·8	198·75	T	Tellurium ..	128	800·00
S	Sulphur....	32	200·00	Au	Gold	196	1225·00
P	Phosphorus	32	200·00	Bi	Bismuth....	210	1312·50
Zn	Zinc	33	206·25				

Comptes Rendus des Travaux de Chimie, vol. i. p. 1.

Observations on Banca Tin, and on the Atomic Weight of Tin. *By* Prof. MULDER.

The author obtained from the Netherlands Society of Commerce samples of Banca tin, to be examined for the government. The object was to obtain from the tin procured from the Banca tin ore a pure tin with the exception of a little iron. The examination of twenty kinds of Banca tin from different mines, and which were imported in different ships, showed them to consist of almost chemically pure tin.

From each of the twenty samples a piece was cut out of the centre, oxidized with nitric acid, and diluted with not too much water before filtration. The loss resulting from the trifling solubility of the tin in the acid liquid was neglected as too unimportant; it contained, besides mere traces of iron, lead and copper, but no silver, antimony or arsenic. The insoluble oxide of tin was calcined and weighed. The results of the analyses are contained in the following table. I. is the kind of tin distinguished by the name of the vessel in which it was brought; II. the quantity of tin employed for examination; III. the amount of oxide of tin obtained from it after oxidation with nitric acid; and IV. the amount of pure tin, calculated upon the supposition that the oxide of tin contains in 100 parts

78·616 tin and 21·384 oxygen.

I.	II.	III.	IV.
1. Jacob Cats	8·597	10·9335	99·99
2. Elise	8·841	11·2630	100·15
3. Prins Hendrik	9·975	12·7130	100·19
4. Zeeland	11·181	14·2720	100·35
5. Cornelia	9·082	11·5500	100·00
6. Lucipara	12·009	15·2750	100·00
7. Prins Frederik	12·706	16·1620	99·99
8. Middelburg	13·443	17·0860	99·92
9. Clara Henriette	9·609	12·2080	99·88
10. Oud Alblas	8·764	11·1520	100·04
11. Doggersbank	10·080	12·8160	99·95
12. Stad Amsterdam	9·196	11·6920	99·95
13. Koningin der Nederlanden	10·174	12·9270	99·88
14. Zeemanshoop	12·185	15·4790	99·87
15. Anna en Elise	9·304	11·8300	99·96.
16. Josephina en Catharina	9·253	11·7590	99·91
17. Flora	8·090	10·2910	100·00
18. Christophorus Columbus	10·518	13·3790	100·00
19. Adm. Jan. Evertse	10·349	13·1660	100·01
20. Doctrina et Amicitia	8·521	10·8300	99·92
	201·877	256·7735	1999·96

From the fourth column we obtain the arithmetical mean 1999·96 : 20=99·998; according to which, therefore, all these samples, considering the small differences of the numbers from each

other, may be regarded as almost chemically pure tin, especially if we bear in mind that a little tin was left in the nitric acid solution. This solution from all the samples, when mixed, deposited, on evaporation nearly to dryness, 0·210 oxide of tin, and about 0·0061 grm. oxide of tin was separated from the residue from the other metals. Now since the sum of the tin taken for the twenty analyses amounted to 201·877 grms. (see column II.), and the amount of oxide of tin obtained therefrom was 256·7735 grms. (see column III.), we find, on adding to the last number the amount of oxide of tin subsequently obtained, that

201·877 grms. tin give 256·9896 grms. oxide of tin.

In the residue from which the last quantity of oxide of tin had been separated, there was found an amount of oxide of iron corresponding to 0·0395 grm. iron. The oxide of lead contained in it corresponded to 0·0257 lead; the amount of oxide of copper to 0·0126 grm. copper. Not a trace of any other metal could be found in the nitric solution, not even on testing it for the presence of arsenic and antimony in Marsh's apparatus. According to the above, Banca tin has the following composition:—

Iron	0·0395	0·019
Lead	0·0257	0·014
Copper	0·0126	0·006
Tin	201·7992	99·961
	201·8770	100·000

From the excesses obtained (see column IV.), we are justified in assuming that the atomic weight of tin requires to be somewhat modified. With respect to the facts ascertained by experiment, there were obtained from 201·8770 Banca tin, which contains 201·7992 pure tin, 256·9896 oxide of tin after separation of the foreign metals; consequently 201·7992 pure tin have absorbed 256·9896 − 201·7992 = 55·1904 oxygen. If we calculate from this the composition of the oxide of tin for 100 parts, we find for 78·524 tin 21·476 oxygen; which would give 731·230 for the atomic weight of tin, whilst Berzelius made it 735·296.

The results above given had another object than to ascertain the composition of the Banca tin, and are consequently not suited, especially on account of the numerous weighings, to establish the atomic weight of tin; but since they indicated that the equivalent of tin was too high, some experiments were made with chemically pure tin, with this especial object in view, by Mulder and Vlaanderen. 100 parts of tin furnished—

	Mulder.	Vlaanderen.	
	a.	*a.*	*b.*
Oxide of tin.....	127·56	127·56	127·43

Vlaanderen, moreover, examined three other kinds of Banca tin, which contained about the same amount of foreign metals as the preceding kinds. Three oxidations of the first kind furnished for

100 parts of Banca tin, 127·750, 127·707, 127·701 oxide of tin; 100 parts of the second kind furnished 127·50, and 100 parts of the third kind 127·69 oxide of tin. These numbers differ very slightly; and from the coincidence of the two analyses designated by *a.* by Mulder and Vlaanderen, these would appear to be most trustworthy, and the atomic weight of tin would be 725·7. As, however, the analysis cannot guarantee the value of 0·7, Mulder proposes, in order to obtain a whole number, to adopt 725, that is $58 \times 12{\cdot}5$, as the atomic weight of tin. The analysis *b.* of Vlaanderen furnished the number 729·2, consequently nearly the same atomic weight as resulted from the above twenty experiments together (731·230). Admitting the equivalent 725, the composition of the oxide of tin in 100 parts would be—

Tin	78·38
Oxygen	21·62

Scheik. Onderzoek., Part v. No. 4. p. 250.

CHEMICAL PREPARATIONS.

On the Preparation of the Hyposulphite of Soda. By M. Faget.

The composition of this salt as met with in commerce is not always the same; it varies according to the process employed in its production. When it is prepared with the bisulphite of soda and sulphur, the product consists of a large quantity of sulphate and but little hyposulphite.

It is best procured by boiling the neutral sulphite with sulphur. However pure the neutral sulphite may be, the hyposulphite will be mixed with a small quantity of sulphate. M. Pelouze explains the presence of this sulphate by the decomposition of the boiling water in the presence of sulphur and the hyposulphite. I have never however been able to detect the least trace of sulphuretted hydrogen, even on boiling the hyposulphite with sulphur for a long time. I should rather explain the presence of this gas by the simultaneous action of the water and sulphur upon the excess of alkaline carbonate which is added to the bisulphite to transform it into the neutral sulphite.

The best process for procuring the neutral sulphite consists in dividing a solution of alkaline carbonate into two parts, saturating one with sulphurous acid gas, and afterwards neutralizing it with the second portion of the carbonate. When a solution of carbonate of soda is saturated with sulphurous acid gas, the liquid not only contains all the gas forming the bisulphite, but also that which the water of the liquid retains in solution. Hence when the first portion is neutralized by the second, we do not obtain a neutral solution, but a mixture containing excess of the bisulphite. It is therefore best to introduce the neutralized liquid into a large flask, to boil it alone at first, and not to add the sulphur which is to convert it into hyposulphite until the excess of sulphurous acid has escaped. In following this plan, almost the whole of the soda is converted into

the hyposulphite. If requisite, the salt may be purified by recrystallization.

M. Plessy adopts a method of purifying the hyposulphite which is also used with great advantage in the preparation of pure carbonate of soda from the impure commercial crystallized carbonate. The salt is melted in its water of crystallization, and the heat is continued so as to evaporate a portion of the water. When the solution cools, the hyposulphite alone crystallizes, the mother-liquor retaining the impurities. If the hyposulphite does not contain any sulphate, it will not, when dissolved in a large quantity of water, precipitate salts of baryta.

I may mention an easy process for determining the identity of the salt. It is based upon the alteration which it undergoes when heated, and consists in ascertaining the weight of the residue obtained by calcination, and examining if it contains sulphur. From 15 to 30 grs. are introduced into a tube closed at one end. The tube is then carefully heated to drive off the water of crystallization; and when the salt is completely dried, the heat is increased, and the tube heated throughout its whole length, so as to expel the volatilized sulphur which has condensed upon its internal surface. On calcination, the hyposulphite yields sulphur, sulphurous acid and a residue of sulphuret and sulphate. When the tube has cooled, it is again weighed. If the salt be pure, the residue should amount to about 44·6 per cent. of the salt. The presence of sulphuret in the residue is easily determined by treating it with water, and adding a drop of solution of subacetate of lead; that of sulphuric acid, by a salt of baryta. Of all the oxysalts formed by sulphur, the hyposulphite is the only one which yields sulphur on calcination. The neutral sulphite of soda (SO^2, $NaO+10HO$), which is inodorous, also yields sulphuret; but on calcination it neither gives sulphur nor sulphurous acid, and the residue which it leaves amounts to 40·5 per cent.—*Journ. de Pharm.*, May 1849.

On the Preparation of Nitrogen. By B. Corenwinder.

The preparation of nitrogen in the laboratory is accompanied by several inconveniences. Of all the processes employed, there is not one which admits of its being obtained quickly and pure, except by the employment of numerous precautions, or the use of very complicated apparatus. This circumstance induces me to publish the method by which I prepare in a few minutes a large quantity of this gas in a state of absolute purity, as I have convinced myself by the experiments subsequently described.

This method is founded on the decomposition of the nitrite of ammonia, which, as is well known, is separated under the influence of heat into nitrogen and water; but as this salt is difficult to prepare, I substitute for it a mixture of alkaline nitrite of potash and hydrochlorate of ammonia—a mixture which consequently contains the elements of the nitrite of ammonia and of the chloride of potassium.

To obtain the nitrite in a suitable state, a solution of caustic potash of 1·38 spec. grav. must be employed, and the nitrous gas derived from the decomposition of 1 part of starch by 10 parts of nitric acid passed into it until the product is decidedly acid; some caustic potash is then added to it in order to render it perceptibly alkaline.

As the nitrite thus prepared may be kept without undergoing any alteration, when it is desired to procure a supply of nitrogen, it suffices to mix 1 vol. of it with 3 vols. of a highly concentrated solution of hydrochlorate of ammonia, to heat the whole in a little flask over some incandescent charcoal, when a disengagement soon results, and continues with perfect regularity.

As it is requisite, in order to obtain the gas pure, that the nitrite should be alkaline, it is evident that a little ammonia must be disengaged at the same time; but no inconvenience results from this, for it is merely requisite to pass the gas through a flask containing some water acidulated with a little sulphuric acid, to remove it.

Moreover, the following experiments leave no doubt as to the purity of nitrogen obtained in this manner:—

1. After having deprived the gas of ammonia in the manner above described, it was collected in a tube containing a mixture of zinc, sulphuric acid and water, consequently where there was a constant disengagement of nascent hydrogen. The experiment was continued for a long time, but not a trace of ammonia was found in the solution. The result was likewise negative with sulphuret of iron and dilute sulphuric acid.

2. I placed in a glass tube, similar to those used for organic analysis, a known weight of copper recently reduced by hydrogen, and subjected it for half an hour to the action of a red heat and a current of the nitrogen washed, and then dried over pumice-stone moistened with sulphuric acid, taking care not to heat the tube until the whole of the atmospheric air had been expelled by the gas. This experiment was repeated several times without any alteration in the external appearance of the copper or any increase in its weight being perceptible.—*Ann. de Chim. et de Phys.*, July 1849.

On the Preparation of Iodide of Potassium. *By* M. Criquelion.

Take—

Iodine	94 parts.
Iron filings	14 ...
Calcined lime	40 ...

First slake the lime in water, then carefully incorporate the iron filings, upon which add the iodine in small portions to the mixture, and triturate until a drop of the liquid produces only an ochreous stain upon starched paper. It is then filtered, the residue mixed with water, and the clear solution precipitated with carbonate of potash. The carbonate of lime is separated by filtration, and the solution evaporated to crystallization.—*Journ. de Chem. Méd.*, iv p. 429.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Products of Distillation of Lactic Acid and of the Lactate of Copper. By M. ENGELHARDT.

WHEN a highly concentrated lactic acid is exposed to a temperature of 266° to 284° F., an aqueous, acid, somewhat empyreumatic liquid distils over very slowly. It is dilute lactic acid. When this temperature has been maintained for a considerable time until no more water passes over, the brownish-yellow residue forms the anhydrous lactic acid of Pelouze, $C^{12} H^{10} O^{10}$. If the boiling is facilitated by rough substances, &c., the hydrated lactic acid can be brought into a state of ebullition at 392° and be distilled without decomposition; but, without this assistance, whilst a portion passes over which increases in amount according to the height of the temperature, the remainder is converted between 356° and 392° into anhydrous acid.

Anhydrous lactic acid dissolves but very sparingly in boiling water, to which it imparts a bitter taste. In the state in which it occurs forming the residue in the retort, it is a solid, amorphous, brownish-yellow mass, which melts even below the boiling-point of water, becomes tenacious on cooling so as to be drawn into threads, possesses an excessively bitter taste, and dissolves in every proportion in spirit and in absolute alcohol. From this solution the anhydrous acid is precipitated by water in flakes, which gradually unite into drops. By prolonged boiling with water, or by long standing exposed to a moist atmosphere, the anhydrous acid is reconverted into the ordinary state. This metamorphosis is very quickly effected by treatment with alkalies and alkaline earths. The anhydrous lactic acid may be exposed to a temperature of 464° F. without experiencing any change; decomposition begins at 482° and is complete at 500°. The products of decomposition (at 500°) are carbonic oxide, with about 3 to 4 per cent. in volume of carbonic acid; further, aldehyde, lactide and citraconic acid, with which is mixed some reproduced lactic acid; no hydrocarbons were found among them, nor could any lactone or acetone, stated by Pelouze to occur among these products, be detected. From 1 to 2 per cent. of carbon remained in the retort.

When, in order to separate these substances, the distillate is mixed with water, aldehyde and hydrated lactic acid dissolve, whilst

another portion sinks to the bottom as a transparent, yellowish, and at first very mobile oil. When left for some time in contact with water, the amount of the oil gradually decreases, and in the course of a few days it has entirely disappeared, leaving behind a few smeary crystals, which likewise dissolve in the course of time. This results more rapidly when a large quantity of water is added, and the whole well shaken or heated. The oil consists of lactide, citraconic acid and some hydrated lactic acid. That no anhydrous lactic acid distils over as such is proved from the fact, that when the contents of the first recipient are allowed to solidify, and are then treated with alcohol, which leaves the lactide undissolved, no lactic acid is precipitated by water from the alcoholic solution.

Aldehyde.—When the distillate, either in the state of liquid or as a crystalline paste, is heated in a water-bath to 212°, and the new product passed into anhydrous æther kept cold, this subsequently yields, on passing ammonia through it, aldehyde-ammonia.

Lactide.—The residue from the preceding treatment, from which the aldehyde has been removed, forms a brownish liquid, which in most cases again solidifies to a crystalline paste, which is thrown upon a filter, washed with cold absolute alcohol, and dried by pressure between bibulous paper. In order to obtain large crystals, it is redissolved in a little boiling absolute alcohol and set aside to cool. What does not crystallize on cooling is lost, from its becoming converted, both by spontaneous evaporation and by heat, into ordinary lactic acid. The crystals appear to belong to the rhombic system, and exhibit great resemblance to those of the protosulphate of iron. Lactide cakes somewhat together at 248°, and can be sublimed, but it proceeds very slowly. At a higher temperature it melts, sublimes more quickly, and furnishes at 500° the same products of decomposition as the anhydrous lactic acid. Lactide also behaves exactly like anhydrous lactic acid towards water, alkalies and alkaline earths. It is reconverted into hydrated acid. It is however more soluble in boiling water than the anhydrous lactic acid, and again separates for the greater part on cooling in small needles. It has neither smell nor taste, but very soon acquires, with the assimilation of water, a strongly acid taste. Lactide, dried *in vacuo*, furnished on analysis—

Carbon	49·87	6	50·00
Hydrogen	5·67	4	5·56
Oxygen	44·46	4	44·44

Citraconic Acid is produced only in small quantity. The alcohol with which the crystals of lactide were washed contains this acid and also lactic acid; it is filtered and distilled; what passes over at 428° is saturated with carbonate of baryta, when the salt, which is perfectly insoluble in alcohol, falls as a crystalline paste. This is dissolved in boiling water, from which solution the citraconate of baryta separates on cooling in beautiful nacreous laminæ, which are obtained of the largest size when the solution is concentrated until a pellicle forms on the surface. The air-dried salt lost at 212°,

14·82, 14·49, 14·93 and 14·29 per cent., or 5 atoms of water. The salt, dried at 212°, furnished—

Carbon	22·57	22·80	10	22·61
Hydrogen	1·81	1·93	4	1·51
Oxygen	18·15	17·40	6	18·09
Baryta	57·47	57·87	2	57·79

Lactic Acid.—This is left, either in the anhydrous or hydrated state, in the retort, in the preceding distillation of citraconic acid.

In one experiment, in which 19·5 grms. of anhydrous lactic acid were exposed to a temperature of 500°, and which was continued for eight hours, the author obtained 12·2 per cent. aldehyde, 14·9 lactide, and 1 per cent. carbon. Several experiments made at the same temperature furnished approximative results. On raising the temperature above 500°, for instance to 572° and higher, the amount of lactide and lactic acid is diminished and that of the aldehyde increased. As the disengagement of gas is far more violent, the gases must be much more carefully cooled, in order to prove directly the increase of the aldehyde. The lactide formed is for the greater part decomposed into aldehyde and carbonic oxide by this temperature, which is much above that of the point of sublimation. The decomposition of the lactic acid is therefore simply as follows:—At first lactide is produced, and this is decomposed at a higher temperature into 2 equivs. carbonic oxide and 1 equiv. aldehyde, $C^4 H^4 O^2 + 2CO = C^6 H^4 O^4$. The presence of carbonic acid and the composition of citraconic acid tend to show that in the distillation there is also a substance containing more hydrogen formed; it was however found impossible to isolate it.

Lactate of Copper exhibits two stages of decomposition on destructive distillation. In the first period, which is situated between 392° and 410° F., carbonic acid and aldehyde appear, with a little hydrated lactic acid, the latter probably arising from the crystals retaining some water of crystallization. The retort now contains metallic copper and anhydrous lactic acid, the decomposition of which between 482° and 500° forms the second period. Lactates with strong bases are decomposed in a different manner. The author recommends the dry distillation of lactates with weak bases for the preparation of aldehyde.—Liebig's *Annalen*, lxx. p. 241.

On the Composition of Stearine. *By* G. Arzbæcher.

Induced by the contradictory statements respecting the composition of stearine in Gmelin's 'Chemistry,' which was the more remarkable as the results had been obtained by some of the most experienced chemists, I made several combustions of stearine prepared from beef and mutton suet.

The stearine was prepared from both suets in the usual manner. Both fats were melted in the water-bath (the beef suet melted at 116°·6, the mutton suet at 122°), and agitated with æther. After cooling, the latter was poured off the crystals, the stearine pressed

between paper, and treated four or five times in the same manner. The substance so prepared, after it had been heated sufficiently long in the water-bath to expel the æther, and the melting-point was found to be constant at 141° with both stearines, was of a dazzling white colour, very friable, and readily reduced to powder. On being submitted to combustion, the result showed that a distinct formula exists for each separate stearine.

The stearine from beef suet furnished—

					Mean.
Carbon.....	78·67	78·62	78·95	78·72	78·74
Hydrogen ..	12·22	12·23	12·22	12·43	12·27
Oxygen	9·11	9·19	8·83	8·85	8·99

The stearine from mutton suet furnished—

					Mean.
Carbon.....	76·18	76·60	76·68	76·57	76·50
Hydrogen ..	12·28	12·17	12·17	12·50	12·28
Oxygen	11·54	11·23	11·15	11·03	11·22

In all the combustions oxygen was employed towards the end; and before the fourth analysis was made, the stearine was again recrystallized from æther, in order to be perfectly sure of its purity. Several grammes, subjected to dry distillation, gave a distillate which, boiled with water, exhibited not the least trace of sebacic acid on testing with salts of silver, lead and mercury.

It will be seen that the analyses of the stearine from beef suet agree perfectly with those of Chevreul and Lecanu, for they found in 100 parts stearine (C=75)—

	Chevreul.	Lecanu.
Carbon	78·78	78·74
Hydrogen	11·77	12·27
Oxygen	9·45	8·99

They must therefore have employed stearine from beef suet for their experiments, whilst Liebig and Pelouze must have analysed stearine from mutton suet, since they found—

Carbon	76·60	76·50
Hydrogen	12·29	12·28
Oxygen	11·11	11·22

In accordance with these results, stearine from beef suet would consist of 1 atom glycerine with 2 atoms stearic acid less 8 atoms HO, and that for mutton suet of 1 atom glycerine with 2 atoms stearic acid minus 4HO. The formula of the first would therefore be $C^{142}H^{134}O^{12}$, that of the latter $C^{142}H^{138}O^{16}$, and the theoretical composition of stearine from—

Beef suet.		Mutton suet.	
C^{142}	78·74	C^{142}	76·21
H^{134}	12·39	H^{138}	12·34
O^{12}	8·87	O^{16}	11·45

100 parts would therefore furnish on saponification—

	Beef suet.	Mutton suet.
Stearic acid	98·15	94·90
Glycerine	8·50	8·23

Liebig's *Annalen*, lxx. p. 239.

On the Constitution of Leucine. *By* Prof. Mulder.

Gerhardt, Laurent and Cahours have found a different composition for leucine than the one formerly arrived at by the author. Gerhardt and Laurent state that Mulder found 1 per cent. carbon less than his formula required; but this is incorrect. The numbers which Mulder published (Bulletin der Neêrlande, 1838, p. 149) give, when they are calculated with the equivalents C=6, H=1, only a loss of $\frac{1}{2}$ per cent.

Gerhardt and Laurent found the subjacent results, which moreover agree with the results obtained by Cahours:—

	G. and L.	Cahours.					
Carbon	54·60	55·19	55·04	54·86	55·10	12	54·9
Hydrogen	9·99	9·96	10·11	9·96	10·17	13	9·9
Nitrogen	..	10·63	10·83	10·89	..	1	
Oxygen	..	..	..	..	..	4	

Were this correct, the author, in his investigations made ten years ago, must have had a very considerable loss of hydrogen; he was therefore induced to make some further analyses, which again have not given so much hydrogen. The results, compared with theory, from leucine produced from albumen by potash, are as follows:—

Carbon	54·9	54·8	55·7	12	55·4
Hydrogen	9·3	9·2	9·2	12	9·2
Nitrogen	10·5	..	..	1	10·7
Oxygen	..	..	..	4	24·7

Three other determinations of the hydrogen in leucine prepared from gelatine with sulphuric acid furnished 9·3, 9·3 and 9·3, leading therefore again to Mulder's old formula $C^{12} H^{12} N O^4$. Mulder then requested M. Rost van Tonningen to examine leucine prepared from albumen. He likewise obtained 9·211 and 9·465 hydrogen, and 55·316 carbon.

According to Mulder's experiments of 1838 (Bullet. *l. c.*, p. 180), nitroleucic acid should have the formula I., whilst according to Gerhardt and Laurent it should be expressed by the formula II.:—

I. $C^{12} H^{12} NO^4 + NO^5$, HO.
II. $C^{12} H^{13} NO^4 + NO^5$, HO.

Now, in 1838, Mulder found for the substance dried over sulphuric acid the results given under I., which correspond best with his formula; for, according to that of Gerhardt and Laurent, 7·2 per cent. hydrogen should have been obtained. A recent analysis made by Vlaanderen (II.) likewise confirms Mulder's formula:—

	I.	II.		
Carbon.....	37·5	37·2	12	37·3
Hydrogen	6·9	6·9	13	6·8
Nitrogen	..	..	2	14·5
Oxygen	..	..	10	41·4

Consequently Mulder's formula, $C^{12}H^{12}NO^4$, must be retained; and indeed its correctness is rendered most probable by Gerhardt and Laurent's numerical results, for they found in two analyses 52·9 and 52·8 carbon, and 9·3 to 9·4 hydrogen. They supposed that these differences from the results calculated according to their formula should be attributed to an admixture of carbonate of ammonia; but carbonate of ammonia becomes in the air $NH^4O+HO+2CO^2$, and contains 10·9 hydrogen; and they ought therefore to have obtained more, and not less, water than from pure leucine. It is very probable that a loss of carbon occurs in Mulder's analysis, especially as leucine is burnt with great difficulty.

It is evident that leucine is anhydrous, from its losing no water when mixed and heated with oxide of lead. The muriatic compound mentioned by Gerhardt and Laurent was prepared by Mulder ten years ago. From the statements he then published, it followed that the atomic weight of leucine, deduced from two experiments, was situated between 1655 and 1608, whilst the number calculated according to the formula $C^{12}H^{12}NO^4$ is 1625.—*Scheik. Onderzoek*, 1849, p. 371.

Observations on the Reduction of the Chloride of Silver. *By* M. Wittstein.

The author has made some comparative experiments on the methods hitherto employed for the reduction of the chloride of silver, for instance with carbonate of potash, caustic potash, caustic potash and sugar, iron, zinc, rosin and caustic lime. He also made some experiments with caustic lime and charcoal, and lastly with charcoal alone.

The reduction of the chloride of silver with charcoal is the most simple, surest and cheapest of all. The following is the mode of operation:—2 parts of chloride of silver are carefully mixed with 1 part of moist charcoal powder, and pressed into a black-lead crucible. Hessian crucibles are not well adapted, because their surface is too rough. The crucible is covered lightly with a piece of tile. On calcination, muriatic acid gas escapes; when no more of this is perceived, the calcination is continued from a quarter to half an hour longer.

As soon as the crucible has become quite cold, the outside is cleansed with a feather from adherent ash, then turned upside down on a sheet of paper. Should anything still adhere to the interior, it is easily removed with a feather. The silver is extracted from the carbonaceous mass by nitric acid of 1·20 spec. grav., of which 3 parts are required for every 2 parts of chloride of silver employed. The carbonaceous powder containing the silver is gradually con-

veyed into a flask in which the nitric acid is contained, and gently heated towards the end. The charcoal powder is not washed too long, as the last portions of the silver adhere so tenaciously to the charcoal that too large an amount of liquid would be obtained. The residual charcoal, which must still contain some chloride of silver, is dried and kept for the next operation.

The impurities contained in the solution of silver derived from the ash are, according to the author, very trifling; and by employing lamp-black instead of charcoal, they may be considerably diminished. If it is desired to obtain the silver in the metallic form, the crucible must be heated to a higher temperature for the silver to run together than is possible in an ordinary furnace.

With respect to the decomposition of the chloride of silver by carbon, the author ascribes it solely to the hydrogen contained in the charcoal; for no chlorine is given off in the operation, but only muriatic acid. It is known that all charcoal contains some hydrogen.—Buch. *Rep.*, vol. ii. p. 1.

On the non-existence of Crotonine. *By* F. Weppen.

According to Brandes' directions for the preparation of crotonine, an alcoholic extract is prepared of croton seeds, the greater portion of the alcohol removed by distillation, and the residue boiled with water and magnesia. The precipitate is then exhausted with alcohol, from which, after filtration, the crotonine crystallizes on evaporation.

The crystals so obtained have, it is true, an alkaline reaction, but cannot be burned completely upon platinum foil and do not neutralize acids. When they are digested with dilute sulphuric acid, a layer of oil separates on the surface, which after sufficient washing dissolves readily in hot alcohol, and communicates to the solution an acid reaction. On cooling, the substance separates from the alcohol partially in a butyraceous state. It dissolves readily in carbonate of soda, and furnishes a soap. The supposed crotonine is consequently nothing more than a magnesia soap with an alkaline reaction.—Liebig's *Annalen*, lxx. p. 255.

On a native Compound of Boracic Acid. *By* M. Ulex.

There is found in the nitre beds of Southern Peru some white kidney-shaped masses, which are there called tiza. The quintal (120 lbs.) fetches from eight to ten dollars. They vary in size from that of a hazel-nut to that of a potato, and resemble in external appearance the aluminite of Halle; but on fracture they appear to consist of white, delicate, silky, crystalline, interwoven fibres, which rapidly absorb water and have a slight saline taste.

In these boulders sometimes fragments of andesite, of quartzose and schistose rocks occur, and always with large rhombic prisms of Brognartine.

The specific gravity of this substance is 1·8. It fuses readily before the blowpipe, with tumescence, to a colourless glass, which

remains clear even after cooling. When moistened with sulphuric acid, it colours the flame green; heated in a glass tube, it gives off water without any acid or alkaline reaction. It is scarcely soluble in cold and with difficulty in boiling water; the solution has an alkaline reaction. It dissolves readily in acids without effervescence. On analysis it was found to contain lime, soda, boracic acid and water, with traces of chlorine, nitric acid and sulphuric acid. The three last constituents were evidently owing to accidental impurities, as chloride of sodium and nitre. The following results were obtained:—

Water.....	26·0	25·8	10 =	90·0	25·92
Lime	15·7	15·9	2	56·0	16·13
Soda	8·8	8·8	1	31·2	8·99
Boracic acid	49·5	49·5	5	170·0	48·96

Assuming the atomic relation between boracic acid and soda to be the same as in borax, the above data lead to the formula—

$$NaO, 2BoO^3 + 2CaO, 3BoO^3 + 10HO.$$

This mineral has most resemblance to that described by Hayes under the name of hydroborocalcite, which occurs in the dry plains of Iquique in company with Pickingerite.—Liebig's *Annalen*, lxx. p. 49.

Researches on the Compound Ammonias. By A. Wurtz*.

Preparation and Properties of Methylamine.—The process by which I obtained this base does not differ from that employed by chemists for preparing ammonia. The perfectly dry hydrochlorate of methylamine is mixed with twice its weight of quicklime, and the mixture introduced into a long tube closed at one end so as to occupy about the half of it; the other half is filled with fragments of caustic potash and a piece of glass tubing fitted to it, which dips under a test-glass filled with mercury. The tube is gently heated at the commencement near the closed end; the gaseous methyle-ammonia displaced by the lime is abundantly disengaged, and passes into the receiver filled with mercury.

Thus prepared, methylamine is a non-permanent gas. At about 32° it condenses into a very mobile liquid. Its odour is strongly ammoniacal. Its density was found to be 1·13; it is therefore a little more dense than the atmosphere; the number found by experiment is slightly higher than the theoretical number, 1·075. This is undoubtedly owing to the circumstance that at the temperature of 77° F., at which the experiments were made, the gas is still too near its point of liquefaction.

The methyle-ammoniacal gas is the most soluble of all the gases hitherto known; at 54° 1 vol. of water dissolves 1040 vols. A higher temperature diminishes the solubility, as was to be expected; at 77° water takes up only 959 times its volume. It is rapidly absorbed by charcoal, like ammonia; it also instantly turns red lit-

* The first part of this paper appeared in this Journal for March 15th of the present year.

mus-paper blue, and diffuses dense white vapours when a glass rod moistened with hydrochloric acid is held near. Like ammonia, it absorbs an equal volume of hydrochloric acid and half its volume of carbonic acid. It is distinguished from ammonia by the following property:—When brought near a lighted candle, it takes fire and burns with a yellowish flame.

The composition of the gaseous methyle-ammonia is represented by the formula $C^2H^5N=4$ vols. This formula is deduced from the following eudiometrical analyses:—

	I.	II.
Methyle-ammonia	23·3	26·5
Oxygen	67·7	71·0
Residue of the combustion	42·0	51·8
Carbonic acid	23·0	26·0
Nitrogen	12·5	14·5
Oxygen absorbed	54·4	59·7

A very elegant and rapid method of analysis consists in heating this gas with potassium in a bent tube; cyanide of potassium is formed and hydrogen disengaged:—

$$C^2H^5N+K=C^2NK+H^3.$$

The solution of methylamine possesses a strong odour of the gas; its taste is caustic and burning. When iodine is mixed with the solution, it is converted into a garnet-red powder; and the liquid, which scarcely acquires any colour, contains the hydriodate of methylamine, IH, C^2H^5N. The red insoluble compound, which is formed under this circumstance, is analogous to the iodide of nitrogen. The salts of magnesia, alumina, manganese, iron, bismuth, chromium, uranium, tin, lead and mercury are precipitated by methylamine as by ammonia. Salts of zinc are at first precipitated white; but the precipitate dissolves in a large excess of the reagent. Salts of copper are precipitated of a bluish-white colour; an excess of the reagent readily dissolves the precipitate, forming a deep blue liquid. The salts of cadmium, nickel and cobalt are precipitated by the solution of methylamine; but an excess of the reagent does not redissolve the precipitate.

Nitrate of silver is entirely precipitated by methylamine; the oxide of silver dissolves readily in an excess of the reagent. When this solution is left to spontaneous evaporation, a black substance separates, which is analogous to fulminating silver; this substance does not explode either when struck or by the action of heat. Chloride of silver dissolves in a solution of methylamine.

Chloride of gold furnishes a brownish-yellow precipitate, which readily dissolves in an excess of the reagent, forming an orange-coloured liquid. A concentrated solution of chloride of platinum gives with methylamine a crystalline deposit of orange-coloured spangles, which consist of the double hydrochlorate of methylamine and platinum.

Preparation and Properties of Ethylamine.—I obtained this base by decomposing the hydrochlorate of ethylamine by lime. The ap-

paratus was arranged precisely in the same manner as described above when treating of the preparation of methylamine, only that as ethylamine condenses readily and is liquid at the ordinary temperature, the tube is passed into a flask surrounded by ice, or still better by a freezing mixture. The ethylamine, set free at a gentle heat, distils over and is condensed in the recipient. In the pure state it is a light, very mobile and perfectly transparent liquid; it begins to boil at 64° F. When a few drops of it are poured upon the hand, it is immediately volatilized, producing a sensation of great cold; it diffuses an excessively penetrating ammoniacal odour; its causticity is comparable to that of potash; it turns red litmus-paper intensely blue. It gives off dense white vapours in contact with hydrochloric acid; each drop of acid poured into it produces a hissing noise as it mixes with the base. Caustic potash and baryta can be kept in it at the ordinary temperature without any alteration taking place. On approaching a lighted body to it, ethylamine takes fire and burns with a bluish flame. It mixes with water in every proportion, evolving considerable heat, and furnishing a solution whose basic properties are precisely similar to those described above under methylamine. I have, however, remarked that the hydrated oxide of copper dissolves less readily in ethylamine than in methylamine. Chloride of platinum is not precipitated by ethylamine.

When a solution of ethylamine is mixed with oxalic æther, it soon becomes turbid; alcohol is produced, and some very delicate crystals of a compound which stands in the same relation to oxamide as ethylamine to ammonia. The composition of this ethyle-oxamide is represented by the formula $C^6 H^{10} N^2 O^2$.

The composition of anhydrous ethylamine is—

	Found.		Calculated.
Carbon	54·4	..	54·3
Hydrogen	15·9	..	15·5
Nitrogen	30·9	31·3	31·2

which numbers lead to the formula $C^4 H^7 N$.—*Comptes Rendus*, August 13, 1849.

On the Products of Decomposition of Aloes by Nitric Acid. *By* Prof. Mulder.

Since Mulder published his investigations on chrysammic and chrysolepic acids, a continuation of Schunck's researches on some products of decomposition of chrysammic acid has appeared*. Mulder observes that not a single result of Schunck's last investigation is confirmed by his experiments, in which he was assisted by Messrs. Vlaanderen and Rost van Tonningen.

The products of decomposition of aloes by nitric acid were prepared and purified, with a few slight modifications, according to Schunck's directions. 1 part of aloes was heated with 8 parts of

* See Chem. Gaz., vol. vi. p. 210.

nitric acid, then removed from the fire until the action ceased, and evaporated until a yellow powder began to separate. After it had cooled, water was added, when a further large quantity of a yellow powder separated, which was washed with water, and then treated with boiling alcohol. The chrysammic acid, which is far less soluble in cold alcohol, is left for the greater part undissolved on cooling; on further evaporating the liquid filtered from it, aloetic acid separates, which still contains some chrysammic acid. On further evaporation, pure aloetic acid separates. Schunck's aloe-resinic acid remains in the brown residual liquid.

Aloetic Acid, $C^{14}H^2N^2O^{10}+HO$, Mulder (according to Schunck $C^{16}H^4N^2O^{13}$).—By repeated solution of the crude product obtained as a yellow powder in boiling alcohol and cooling, &c., this acid is obtained free from chrysammic acid, aloe-resinic acid, and all the other substances contained in the aloes insoluble in nitric acid. It then forms a crystalline orange-yellow powder, which is slightly soluble in cold, more soluble in boiling water, and pretty soluble in alcohol. It bears considerable resemblance to chrysammic acid, but is far more soluble in water and alcohol; never of so pure a yellow or greenish-yellow as that, but more of an orange colour. It forms with potash and soda very soluble salts, by which means it can readily be distinguished and separated from the salts of chrysammic acid. It forms insoluble salts with baryta and oxide of lead. It dissolves readily in solution of ammonia to a beautiful violet liquid: the action of ammoniacal gas upon this acid is highly remarkable, as will be subsequently shown. The amount of water (1 atom) and the composition of the acid are deduced from the following analyses of the acid and its salts, which differ from those of Schunck. It differs from chrysammic acid $=C^{14}HN^2O^{11}+HO$ by $+H-O$. Boiling nitric acid deprives aloetic acid of 1 atom H, and yields to it 1 atom O when chrysammic acid is formed. The acid, dried at 248°, furnished M. Vlaanderen with—

Carbon.....	41·6	41·5	41·5	14	= 1051·68	41·4
Hydrogen....	1·5	1·7	1·4	3	37·45	1·5
Nitrogen	14·4	14·5	14·5	2	350·00	13·8
Oxygen	42·5	42·3	42·6	11	1100·00	43·3

Aloetate of Baryta, $BaO, C^{14}H^2N^2O^{10}$.—Aloetic acid diffused in water is digested with a dilute, hot, aqueous solution of acetate of baryta in excess; the nearly insoluble baryta salt washed with water and dried at 248° yielded 27·4 and 27·2 per cent. baryta. The quantity required by the above formula is 28·3. The salt was burnt, when it gave for the acid—

Carbon	42·7	42·5	14	= 1051·68	43·3
Hydrogen ..	1·7	1·3	2	24·96	1·0
Nitrogen ..	13·5	13·6	2	350·00	14·4
Oxygen....	42·1	42·6	10	1000·00	41·3

Aloetate of Lead, $2PbO, C^{14}H^2N^2O^{10}$.—The preceding baryta salt precipitated with acetate of lead, furnishes a dark red insoluble

precipitate very similar to the chrysammate of lead. It was found to contain 54·5 per cent. oxide of lead; the formula requires 53·5.

Aloetinamide, $C^{14}H^5N^3O^{10}$.—It has already been stated above that aloetic acid is dissolved by ammonia with a violet colour. Treated with pure ammoniacal gas at the ordinary temperature, or even some degrees below freezing-point, it explodes, leaving a black mass insoluble in water, ammonia, alcohol and potash, and in which Vlaanderen found 68·1 carbon and 1·6 per cent. hydrogen. Chrysammic acid does not behave in the same manner. This explosion may be prevented by diluting the ammoniacal gas with a large quantity of atmospheric air; the substance acquires a dark violet colour, and water is eliminated. The whole of the combined water is not expelled at 212°. It furnished on analysis, after having been dried at this temperature—

Carbon	39·16	14 =	1051·68	39·8
Hydrogen	2·54	5	62·40	2·4
Nitrogen.....	20·58	3	525·00	19·9
Oxygen	37·72	10	1000·00	37·9

It differs from chrysamminamide, $C^{14}H^4N^3O^{11}$, by its much greater solubility in water, its darker violet colour, and in composition by $+H-O$. Even when dilute ammonia is mixed with aloetic acid, this amide is formed. Nitric or muriatic acid instantly convert it into aloetic acid and ammonia.

Hydro-aloetic Acid, $C^{14}H^4N^2O^{11}$, or $C^{14}H^3NO^{11}NH^2$ (anhydrous).—This acid is formed whenever aloetic acid or chrysammic acid is brought into contact with water and protochloride of tin; and the employment of chrysammic acid as a pigment is based on the production of this acid. Exposed to the air, or even in closed vessels, protochloride of tin gradually separates from the above acids an insoluble violet compound, which therefore produces this colour when fabrics mordanted with protochloride of tin are dyed with chrysammic acid.

This compound is best prepared by treating chrysammic acid with water and an excess of protochloride of tin; a heavy dark violet powder is formed which is quite insoluble in the liquid; it was washed and dried at 248°. This salt has the following composition:—

Carbon	19·3	..	14 =	1051·68	19·5
Hydrogen ..	1·1	..	4	50·00	0·9
Nitrogen....	6·4	..	2	350·00	6·6
Oxygen	21·2	..	11	1100·00	20·6
Oxide of tin..	52·1	51·9	3	2805·90	52·4

The organic substance combined with the oxide of tin, SnO^2, differs by H and HO from the anhydrous aloetic acid; it differs essentially in its properties, and it certainly contains amide. It is formed from chrysammic acid as follows:—

$$C^{14}H^2N^2O^{12}+3SnCl+5HO=C^{14}H^4N^2O^{11}+3SnO^2+3HCl.$$

When moistened with potash this tin salt is coloured violet-blue with disengagement of ammonia. From this circumstance, and

from aloe-resinic acid having the composition $C^{14}H^{3}NO^{12}$, it might be suspected to be an amidogen compound of this acid $= C^{14}H^{2}NO^{11} + NH^{2}$; but the brown colour of the aloe-resinic acid is not altered by ammonia. This hydro-aloetic acid is consequently perfectly distinct from what Schunck has considered to be hydrochrysammide, $C^{14}H^{6}N^{2}O^{6}$. Nothing can be concluded from the blue colour of the products which are formed from chrysammic acid, as it furnishes a large number of that colour.

When heated with strong nitric acid, the tin salt of the hydro-aloetic acid furnishes oxide of tin with disengagement of nitrous vapours and a red colouring of the liquid. This red colouring first makes its appearance owing to the production of the more soluble salt of aloetic acid. On further ebullition chrysammic acid is reproduced simply by the oxidation of H and H^{2}, as will be evident from the formulæ. We have—

Anhydrous hydro-aloetic acid.....	$C^{14}H^{4}N^{2}O^{11}$
Hydrated aloetic acid	$C^{14}H^{3}N^{2}O^{11}$
Anhydrous chrysammic acid	$C^{14}H\ N^{2}O^{11}$.

When potash is added after mixing the hydro-aloetate of tin with nitric acid, soluble aloetate of potash is obtained. If it is now again boiled with nitric acid, and more potash added in excess, the sparingly soluble chrysammate is produced.

Chrysammide, $C^{14}H^{4}N^{3}O^{11}$ (Mulder).—What Schunck has regarded under the name of chrysamminamide as an amide of chrysammic acid, appears on comparing his analyses with the calculated numbers to have been a combination of Mulder's chrysammide with ammonia. Mulder had already alluded to a combination of this substance with oxide of lead, and a similar one exists with oxide of ammonium, which is decomposed at 212°, giving off water and ammonia.

		Calculated.	Schunck.	
Carbon	14	38·6	37·61	37·88
Hydrogen	4	1·8	2·35	2·21
Nitrogen.....	3	19·3	19·72	19·87
Oxygen	11	40·3	40·32	40·04

Further, the substance called amidochrysammic acid by Schunck is a mixture of chrysammide and green chrysammic acid. Several definite combinations of these two substances exist; the most simple one is $C^{14}H^{4}N^{3}O^{11} + C^{14}H^{2}N^{2}O^{12}$. But this compound has nothing in common with Schunck's amidochrysammic acid, nor with its barytic compound. It is doubtful whether in Schunck's baryta salt there was any chrysammide present; for if chrysammide is dissolved in water and chloride of barium added to it, no precipitate is obtained. On boiling, it is true, a dark red powder falls which is likewise obtained by adding ammonia to the mixture of chrysammide and chloride of barium at the ordinary temperature; but the two red precipitates are not identical. In the first case, when the boiling has been continued sufficiently long, chrysammate of baryta and chloride of ammonium are produced; in the latter case there is formed

chrysammide-baryta and chloride of ammonium. The chrysammide resembles very closely the chrysammate of baryta; but it is readily distinguished from it by its more violet than light red colour, and by its disengaging ammonia when treated with potash.

The compounds of chrysammide do not bear a temperature of 212°; those with two equivalents of base lose the whole of the ammonia, as the lead compound, which leaves chrysammate of lead; those with one equivalent base frequently retain some ammonia.

[To be continued.]

Method of cleaning Vessels and other Articles of Silver.

Boil 30 grms. of finely pulverized and calcined hartshorn in a quart of water, and while on the fire put as many silver articles in the vessel used for boiling as it will hold, and leave them there for a short time; then withdraw them, and dry them over the fire. Continue this until all the articles have been treated in the same manner. Then introduce into the hartshorn water clean woollen rags, and allow them to remain until saturated; after which dry them, and use them for polishing the silver. This is also the best substance which can be employed for cleaning locks and brass handles of room doors. When the silver articles are perfectly dry, they must be carefully rubbed with a soft leather. This mode of cleaning is excellent, and much preferable to the employment of any powder containing mercury, as mercury has the effect of rendering the silver so brittle as to break on falling.—*Technologiste*; and Newton's *Journal*, May 1849.

Observations upon the Composition of a Calculus from a Monkey's Liver. By Thornton J. Herapath.

The animal which formed the subject of this observation was a favourite male monkey, lately in the possession of my friend C. T. Coathupe, Esq., of Wraxall House near Bristol. It having died suddenly, after a short illness, a post-mortem examination of the body was instituted by Mr. Coathupe; when, amongst other morbid appearances, it was found that the two principal lobes of the liver had become connected together, and at the point of junction a cyst had been formed, which contained a small calculus of an elongated oval form. This calculus, when first extracted, was soft to the touch, but it speedily became hard upon drying. It weighed about half a grain, and consisted of a white pulpy substance, enclosed in a somewhat fibrous or membranous external covering. When dry, the white interior portion, which was perfectly amorphous and exhibited not the slightest traces of a crystalline structure, was easily removed by the point of a penknife from the hardened epidermis, and was then found to possess the following properties:—Heated to redness upon platina foil, it turned black, and afterwards burnt with a smoky flame, exhaling the odour of burnt

horn or feather. The white ash which remained behind was almost entirely soluble in diluted nitric and hydrochloric acids, with considerable effervescence; and the acid solution yielded, upon the addition of an excess of ammonia, a white bulky precipitate, which was completely redissolved by acetic acid. Oxalate of ammonia and phosphate of soda furnished the usual indications of lime and magnesia.

Boiling alcohol and æther extracted a small quantity of fat from the original calculus, and water afterwards removed a trace of chloride of sodium. Acted upon by diluted hydrochloric acid, the earthy salts, which formed about half the entire weight of the calculus, were extracted, leaving a bulky residue of albumen. This, when treated with strong nitric acid, was turned of a yellow colour, which behaviour would appear to point out the presence of fibrine.

Its quantitative analysis was as follows, but the calculus was of too small a size to enable me to determine its composition with any great degree of accuracy:—

Water	a little
Albumen, with a little fibrine and fatty matter	0·178
Phosphate of lime, with traces of phosphate of magnesia	0·094
Perphosphate of iron	exceedingly minute traces
Carbonate of lime, with some carbonate of magnesia	0·068
Chloride of sodium	traces
Epidermis and loss	0·160
	0·500

Mansion House, Old Park, Bristol,
August 26th, 1849.

ANALYTICAL CHEMISTRY.

Observations on the Employment of the Sesquibasic Phosphate of Silver in Mineral and Organic Analysis for decomposing the Alkaline and Earthy Chlorides. *By* J. L. Lassaigne.

Chenevix was the first to advise the use of the sesquibasic phosphate of silver for separating the chloride of barium from the chlorate of baryta in the preparation of the latter salt. It is by means of this process, now nearly abandoned, that this salt was first obtained in the state of purity, and that chemists were enabled to study its principal properties.

The decomposing action which the hydrated sesquibasic phosphate of silver exerts on the alkaline and earthy chlorides induced me to use this metallic salt, first, to isolate certain nitrates from alkaline and earthy chlorides; and secondly, for the separation of the saccharine principles mixed with chloride of sodium, as they occur in certain organic products.

I applied the first method to the analysis of a well water. It is well known that the salts soluble in strong alcohol consist principally of chlorides of magnesium and calcium, frequently associated with

nitrates in greater or less quantity. Wishing to ascertain the relation between the nitrate of magnesia and chloride of magnesium contained in a mixture obtained by alcohol from the residue of a well water from the neighbourhood of Paris, I tried the hydrated phosphate of silver upon the solution of these two salts; and was soon convinced that, with the assistance of a gentle heat, the chloride of magnesium is entirely converted into insoluble chloride of silver and subphosphate of magnesia, whilst the nitrate remained in solution and could be procured by evaporation. This simple method may therefore be applied in a number of circumstances; it also answers for a mixture of nitrate of lime and chloride of calcium. However, a minute quantity of phosphate of silver is held in solution by the alkaline nitrate; but this quantity is exceedingly small, and may easily be taken into account in a quantitative analysis. The separation of an earthy nitrate from a chloride is best effected by evaporating to dryness the solution in which an excess of the hydrated phosphate of silver has been suspended, and then treating the residue with cold distilled water, in order to isolate the insoluble products formed by filtration.

It is by operating in this way that I have been able to determine in a direct manner the minute quantity of nitrate of magnesia which was mixed with chloride of magnesium in the residue of the well water. This process may be advantageously used in the analyses of mineral waters for effecting analogous separations.

The phosphate of silver may also be employed for the isolation of cane- and grape-sugar when mixed with a small quantity of chloride of sodium. These two substances, soluble in alcohol, sometimes occur together in certain organic products. By the action of the phosphate of silver on a solution of such a mixture, there is formed at the ordinary temperature insoluble chloride of silver and soluble phosphate of soda, which remains mixed with the sugar. Now the phosphate of soda being insoluble in alcohol of 0·869 spec. grav., whilst the sugar on the contrary is soluble in it, it is possible to effect their separation by acting with alcohol on the product evaporated to dryness. Direct experiments showed that cane- and grape-sugar isolated by this method contained not a trace of the chloride of sodium which had been intentionally mixed with them. By acting in the cold and quickly on the soluble principles, in order to isolate them from the chlorides which they may contain, no fear need be entertained of the reducing action of the organic substances on a portion of the phosphate of silver.—*Comptes Rendus*, Aug. 13, 1849.

On the Separation of Nickel and Cobalt. By Prof. Wöhler.

In Liebig's excellent method* of separating quantitatively nickel and cobalt by converting the two metals into potassio-cyanides, and then precipitating the nickel by peroxide of mercury, the proto-nitrate of mercury may be subsequently used for conveniently pre-

* Chem. Gaz., vol. vi. p. 145.

cipitating the cobalt and determining its weight directly. The liquid from which the nickel has been precipitated by peroxide of mercury, and which contains the cobalt in the state of cobalticyanide of potassium, is carefully neutralized with nitric acid and as neutral a solution as possible of the protonitrate of mercury added. The whole of the cobalt is precipitated as cobalticyanide of mercury in the form of a heavy white precipitate, which is readily filtered and washed. It then merely requires to be heated with access of air to convert it into black oxide of cobalt.—Liebig's *Annalen*, lxx. p. 256.

Observations on the Estimation of Nitrogen according to Dumas' *Method. By* Prof. Mulder.

The author observed, in determining nitrogen according to this method, that when substances containing a very large amount of carbon and hydrogen were analysed, a gas which burnt with a blue flame (carbonic oxide) was formed. This took place notwithstanding the greatest precaution in conducting the analysis. The cause of this production of carbonic oxide was owing to the circumstance, that the carbonic acid which is disengaged from the bicarbonate of soda after the combustion, is reduced to carbonic oxide on passing over the incandescent unconsumed carbon. This carbonic oxide is not reconverted by the oxide of copper into carbonic acid, because the disengagement of the carbonic acid intended to expel the nitrogen is generally not sufficiently slow, and the carbonic oxide is carried away by the rapid current of carbonic acid.

But even when the carbonic acid was very slowly disengaged at the commencement, this evolution of carbonic oxide still occurred. It is therefore necessary to attend to this the more, as experience has sufficiently shown that some bodies cannot be perfectly burnt without oxygen. These, therefore, inasmuch as they leave a residue of carbon when treated according to Dumas' method for estimating the nitrogen, must furnish carbonic oxide, which mixes with the nitrogen, and renders the determination of its amount erroneous. In such cases a more intimate mixture of the substance to be analysed with the oxide of copper is advisable, and also to let the carbonic acid disengaged towards the end of the combustion from the bicarbonate of soda pass at first very slowly over the oxide of copper, in order that the carbonic oxide may be converted into carbonic acid. —*Scheik. Onderzoek*, 1849, p. 377.

On the Detection and Estimation of Phosphoric Acid. By C. Lecomte.

The detection of phosphoric acid by the reagents hitherto employed is accompanied with considerable difficulty. Having examined the behaviour of almost all the known oxides towards phosphoric acid, the phosphate obtained with the oxide of uranium was

found to exhibit a great superiority over all the others with respect to its almost absolute insolubility in water and the rapidity with which it is deposited, leaving the liquid perfectly transparent.

Numerous experiments have demonstrated the certainty with which the soluble salts of uranium detect the presence of phosphoric acid wherever they meet with it. The two following facts, confirmed a large number of times, may suffice to prove this.

I. 0·05 grm. of syrupy phosphoric acid added to 4 litres of distilled water furnished with nitrate of uranium a very copious precipitate on ebullition; salts of soda, potash, ammonia, lime and magnesia (in the two last cases the liquid was acidulated so as to keep it transparent) added to the preceding liquid do not prevent the precipitate being formed; the same salts added to distilled water do not precipitate the nitrate of uranium.

II. Phosphate of lime dissolved in hydrochloric acid and the liquid highly diluted, furnished a very copious precipitate with it.

The determination of the amount of phosphoric acid in the soluble phosphates is very simple. A solution of nitrate of uranium is made, each cubic centimetre of which precipitates 0·001 grm. of phosphoric acid; a known weight of the phosphate for analysis is taken and dissolved in a known volume of distilled water, carefully neutralizing; 50 cub. centim. of this liquid are heated to boiling in a small flask, and the nitrate of uranium poured into it from a graduated burette until the liquid above the precipitate is perfectly clear, taking care to boil it for a second after each addition of the normal solution.

In a subsequent paper I shall describe a process for the estimation of phosphoric acid in the insoluble phosphates by means of the nitrate of uranium.—*Comptes Rendus*, July 16, 1849.

PATENTS.

Patent granted to Hugh Lee Pattinson *for Improvements in Manufacturing certain Compounds of Lead.*

The patentee commences his specification by stating that he has discovered that when $\frac{1}{2}$ an equivalent or thereabouts of lime, soda, potash, ammonia or barytes is added to 1 equiv. of chloride of lead, both in solution, the whole of the lead is precipitated as a definite compound of 1 atom of chloride of lead and 1 atom of hydrated oxide of lead, which, when dried at 212° F. or under, has the composition just stated, or PbCl + PbO, HO; but when dried at a temperature varying from 212° to 350° it loses more or less of the atom of water, and becomes or approaches to PbCl + PbO. If less than $\frac{1}{2}$ an equiv. of the alkaline precipitant is employed, the same definite oxychloride of lead is precipitated, but some of the chloride of lead

remains in solution. The oxychloride of lead thus produced possesses a brilliant white colour and great "body" qualities, which render it an excellent pigment and useful for most purposes to which white lead is applicable.

The invention consists in the manufacture and application of this oxychloride of lead, or such other compounds of oxide of lead and chloride of lead as shall result from the following mode of manufacture:—The patentee states that lime will answer as well for the purposes of this invention as any of the other alkaline precipitants above named, and he prefers to use it on account of its cheapness. He first makes a saturated lime-water, by throwing an excess of slaked lime into a tub, filling the tub with water, and allowing it to stand until it becomes clear. The clear liquor will contain in from 770 to 780 parts 1 part of lime; and therefore 1 cubic foot of it will contain 567 or 568 grs. of lime. A solution of chloride of lead is then made by dissolving it in boiling water, in the proportion of 1 lb. of pure chloride of lead to $1\frac{1}{2}$ cubic foot of water. As some water contains earthy salts (sulphates or carbonates, or both) which precipitate lead, the patentee prefers to use such an excess of chloride of lead as will compensate for this loss. The solution is prepared by introducing the chloride of lead and boiling water into a wooden barrel, provided with a revolving agitator, and then it is run into cisterns to settle. The clear solution of chloride of lead is mixed while still warm (because if allowed to become cool it would deposit some of the chloride of lead) with an equal bulk of the lime-water; on this taking place, the insoluble oxychloride of lead is immediately formed and speedily settles to the bottom of the cistern, leaving a clear supernatant liquor (a weak solution of chloride of calcium); and after this liquor is drawn off the precipitate is collected and dried.

As the operation of mixing the lime-water and the solution of chloride of lead requires to be performed in an instantaneous manner, the patentee prefers to employ for this purpose two tumbling boxes, of about 16 cubic feet capacity, which are charged with the two liquids and simultaneously upset into a cistern, in which the oxychloride of lead is instantaneously formed, and from which the mixture flows into other cisterns, where the oxychloride subsides.

The patentee states, that although he has only mentioned pure crystallized chloride of lead in the description of the process, yet it is not absolutely necessary that it should be in this form; for a rough chloride, made from lead ore and its equivalent of muriatic acid, boiled to dryness, will answer, provided it be well washed, to free it from chlorides of iron, manganese, or other bodies likely to injure the colour of the oxychloride. The exact proportion of pure chloride contained in the rough chloride should be ascertained previous to use, in order that the proper quantity may be mixed with the lime-water. If, however, a solution of chloride of lead of uncertain strength is obtained, or lime-water not quite saturated, they can be used with but little disadvantage; for it is only necessary to

be careful not to add an excess of lime (*i. e.* not more than the half equivalent), which can be easily ascertained after a few trials, by filling the lime or lead tumbling box more or less with its respective solution, as the trials may direct.

The patentee says that it will not be necessary to describe any particular mode of proceeding with soda, potash, ammonia or barytes; for if ever it should happen that these bodies could be used in preference to lime, it would be merely necessary to make a solution of each of known strength, and to use it with chloride of lead in the same manner as the lime-water.—Sealed Feb. 14, 1849.

Patent granted to Jean Adolphe Carteron, *for certain Improvements in Dyeing.*

These improvements in dyeing consist in the preparation of certain mordants, to be used instead of the cream of tartar and cream of tartar and alum now commonly employed, whereby colours will be produced at less cost than heretofore, and of superior brilliancy and variety.

The mordants are four in number. The first is prepared by dissolving 18 parts by weight of common salt and 9 parts of tartaric acid in 67 parts of boiling water, and then adding 18 parts of the acetic acid of commerce. One pound of this mordant is equivalent for dyeing purposes to about one pound of cream of tartar, and it is used in the same manner. It is suitable for crimson and all reddish dyes.

The second mordant is made by triturating and mixing 1 part of alum with 2 parts of the residuum (sulphate of soda) of that mode of manufacturing nitric acid in which nitrate of soda is employed. $2\frac{1}{4}$ lbs. of this mordant are equivalent to half that quantity of cream of tartar, and it is to be used in the same way. It is suitable for all olive and brown dyes.

The third mordant is prepared by triturating and mixing together 5 parts of common salt and 1 part of the residuum of the manufacture of sulphuric acid where nitrate of potash is employed. This mordant is to be used in the same proportions to cream of tartar as the second mordant, and it is applicable to black and dark colours only.

The fourth mordant is formed by dissolving 6 parts of sulphate of alumina, 3 parts of nitric acid and 1 part of caustic ley of 24° Beaumé in 20 quarts of boiling water. It may be used in dyers' baths for green dyes of all shades and fancy dyes, in the proportion of 1 pint for every 20 lbs. weight of the fabrics to be dyed.—Sealed Feb. 5, 1849.

THE CHEMICAL GAZETTE.

No. CLXVII.—October 1, 1849.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Oxidation of Organic Compounds. By Prof. Liebig.

In the experiments of Messrs. Schlieper and Guckelberger*, on the oxidation of gelatine, caseine, albumen and fibrine, one of the most remarkable and constant products obtained was an ætherial liquid, valeronitrile, which contains the elements of the valerianate of ammonia, from which the elements of water (and with it all the oxygen of the acid) have separated.

The formation of this substance, containing nitrogen but *no oxygen*, by a process of oxidation, is certainly a most unexpected fact; and it appeared not uninteresting to submit its production to a more minute examination. As is well known, the above-mentioned animal substances are completely decomposed by caustic alkalies, as well as by acids, with the assistance of heat. From Bopp's investigation†, it results, that in both processes of decomposition two nitrogenous compounds, tyrosine and leucine, are obtained from fibrine, albumen and caseine; whilst by the action of acids and alkalies upon gelatine, leucine and glycocoll are produced. Leucine and tyrosine are likewise formed in the putrefaction of albumen, fibrine and caseine. The constant formation of these substances by three such different modes of decomposition leads to the supposition that albumen, fibrine and caseine are conjugate compounds, which contain as conjuncts, among others, leucine and tyrosine. In the same manner, glycocoll, or a compound which on the assimilation of the elements of water produces glycocoll, appears to be a conjunct of gelatine.

The greater proportion of the other products which originate by the action of acids and alkalies, as well as by putrescence from the above animal substances, contain no nitrogen; they are organic acids, such as butyric, valerianic, metacetonic and acetic acids. Butyric acid forms the principal constituent. In Bopp's experiments, several pounds of pure anhydrous butyric acid were prepared by the *putrefactive* decomposition of animal substances.

From all the animal substances submitted to oxidation, M. Guckelberger obtained among the non-nitrogenous products, in unequal proportions, butyric, caproic, valerianic, metacetonic, acetic and

* Chem. Gaz., vol. vi. pp. 89, 114.

† Page 158 of the present volume.

formic acids, several aldehydes, for instance the aldehydes of acetic, butyric and metacetonic acids, and oil of bitter almonds. The nitrogenous substances consisted of prussic acid and valeronitrile. The residue of the distillation of these animal substances with sulphuric acid and manganese contained neither leucine nor tyrosine.

Regarded as conjugate compounds, albumen, fibrine and caseine would consist of a group of nitrogenous substances, which, on the addition of the elements of water and of *oxygen*, are separated into ammonia, leucine, tyrosine (in the case of gelatine, into glycocoll), or into ammonia, valeronitrile and prussic acid, and into aldehydes or organic acids. The above products originate in a mixture which contains manganese or chromate of potash and *free sulphuric acid*; and it is highly probable that a separation of the albumen, caseine, fibrine and gelatine by the action of the acid into ammonia, leucine, tyrosine, glycocoll, and on the other hand into certain non-nitrogenous products, precedes the oxidation, just as would happen if no manganese were present. On both suppositions valeronitrile and prussic acid would be secondary products of decomposition formed by the action of the acids in the presence of oxygen upon one or the other of the solid and non-volatile nitrogenous products, leucine, tyrosine or glycocoll, resulting from the action of alkali, acids or putrefaction.

This view has been completely confirmed with respect to valeronitrile, and probably with regard to the prussic acid.

When leucine (Gmelin's oxide of caseine, the aposepedine of Proust) is distilled with dilute sulphuric acid and manganese, valeronitrile and carbonic acid are obtained as volatile products. On employing a more concentrated acid, the distillate is sour, from the presence of valerianic acid; and in this case the residue contains ammonia. Consequently, on the addition of oxygen, the leucine separates into valeronitrile, carbonic acid and water.

According to the experiments of Bopp, tyrosine furnishes no nitrogenous volatile products on treatment with oxidizing agents.

Glycocoll, treated with dilute sulphuric acid and manganese, is decomposed into prussic acid, carbonic acid and water. The prussic acid represents the nitrile of formic acid. It is produced from the formiate of ammonia in the same way as the benzonitrile from benzoic acid.

Leucine experiences a totally different kind of decomposition by peroxide of lead, *i. e.* by the addition of oxygen, in the absence of an acid. In this case mere traces of valeronitrile are obtained; the principal product is the butyric aldehyde* obtained by Guckelberger, an ætherial oily compound, pretty soluble in water, and which is highly remarkable from its property of forming with ammonia a beautiful crystalline compound, which is very sparingly soluble in water. On the first action of the peroxide of lead, valeronitrile

* The butyric aldehyde obtained on this occasion furnished on analysis—

Carbon	67·3	6	66·7
Hydrogen	11·4	6	11·1
Oxygen	...	3	22·2

passes over, then a quantity of butyric aldehyde, and lastly ammonia, which produces the ammoniacal compound in the recipient, in consequence of which the distilled oily liquids solidify into a crystalline mass. I have previously shown, that by melting leucine (which contains the elements of cyanic acid, amylic æther and water) with hydrate of potash, valerianic acid, hydrogen and ammonia are obtained; and with a more powerful action of the alkali, butyric acid, ammonia and hydrogen.

With regard to the non-nitrogenous products, which the above animal substances furnish in the different processes of oxidation, it can scarcely be assumed that each of them originates from a separate conjunct, forming a constituent of the albumen, fibrine or caseine; otherwise we must admit as many conjuncts as there are different products obtained. The one series of these products belongs to a class of acids whose relation to and connexion with each other is unmistakeable. The valerianic, caproic, butyric, metacetonic, acetic and formic acids are members of the series $(C^2\,H^2)^n\,O^4$; and all the observations hitherto made leave no doubt that from one of these acids a higher order, or from a more complex radical by the simple addition of oxygen, acids with a more simple radical may be produced. Redtenbacher* obtained, in his important investigation on the products of oxidation of oleic acid (an acid which does not belong to the series $2(CH)^n + O^4$), eight acids (of which one proved to be new), which are members of this series, viz. acetic, metacetonic, butyric, valerianic, caproic, œnanthylic, caprylic and pelargonic acids; and Dr. Schneider† furnished a decisive proof that a large number of these acids may be obtained by a process of oxidation from substances containing no oxygen, as the oily hydrocarbons produced in the destructive distillation of fats. From the purified product of the distillation of oleic acid, which contains carbon and hydrogen in the proportion of 6 : 5, Schneider procured, by treatment with nitric acid, œnanthylic, caproic, valerianic, acetic and metacetonic acids. On employing chromic acid (a mixture of bichromate of potash and sulphuric acid), he obtained, on the other hand, only acetic and metacetonic acids. The acids of the series above the metacetonic acid, if indeed any were produced, as valerianic acid, &c., had been converted into acids containing more oxygen by the chromic acid.

Several views may be entertained respecting the mode in which, by the assimilation of oxygen, acids of a complex radical are converted into compounds of a more simple kind. With the same amount of carbon and hydrogen, butyric acid contains only half as much oxygen as acetic acid, caproic acid half as much as metacetonic acid, butyric acid half as much as caprylic acid; and it is very probable, that, by the simple addition of a quantity of oxygen equal to that they contain, caprylic acid may be converted into butyric acid, caproic into metacetonic, and butyric into acetic acid.

* Chem. Gaz., vol. iv. p. 285.

† Page 334 of the present volume.

This view, simple as it is, has no foundation in fact. If we take into consideration those observations which have been made on the oxidation at low temperatures of these fatty acids which are mostly volatile without change, a different explanation of this transition of one acid into the other must be preferred; and I believe that the law of this metamorphosis has been satisfactorily explained and established by the investigations of Dr. Kolbe on the electrolysis of organic compounds. Kolbe found that when 1 equiv. of oxygen is added to the elements of valerianic acid, considered to be anhydrous, 2 equivs. of carbonic acid separate from it, and a hydrocarbon is obtained, which he calls valyle:—

Anhydrous valerianic acid	$C^{10} H^9 O^3$
Add to which 1 oxygen	O
	$C^{10} H^9 O^4$
Deduct 2 atoms of carbonic acid ..	C^2 O^4
And there remains valyle	C^8 H^9

The same chemist has shown, in his interesting memoir, that valyle is converted by the assimilation of oxygen into butyric acid; and has rendered it highly probable that in the same process of oxidation, oxide of valyle, and perhaps the hydrate of this oxide (compounds which correspond to the æther and alcohol of butyric acid), are formed, and the transition of valyle into butyric acid appears accordingly to take place through the intervention of several intermediate members, among which perhaps should be reckoned the aldehyde of butyric acid, which is isomeric with the butyrate of the oxide of valyle.

Kolbe obtained, as secondary product of decomposition in this process of oxidation, a gaseous hydrocarbon, which has the same percentage composition as olefiant gas, but twice as high a specific gravity, the formation of which from valyle must be explained by the separation of 1 equiv. of hydrogen in the form of gas, or an oxidation of this hydrogen into water.

Kolbe showed that the transformation of acetic acid into the last member of the series, formic acid, is effected in a perfectly similar manner by electrolysis. 1 equiv. oxygen is added to the elements of anhydrous acetic acid; and it separates into carbonic acid, gaseous methyle and oxide of methyle, which we know is converted by the further assimilation of oxygen into formic acid.

By Kolbe's process, which is a process of oxidation taking place within a liquid at *the ordinary temperature*, we have obtained all the intermediate members, which are formed on the absorption of oxygen by an organic acid, and their conversion into the final products, carbonic acid and water.

The general expression of Kolbe's investigation is the following:—When oxygen is added to the elements of an organic acid containing oxygen, the acid splits up into carbonic acid, which contains the oxygen of the acid, and into a hydrocarbon which contains its carbon.

In consequence of the oxidation of the hydrocarbon, an oxide of it is formed, or the hydrate of this oxide, which is converted, by the replacement of a portion of its hydrogen, into an aldehyde—with more oxygen, into an acid, which by the further addition of oxygen experiences another resolution into carbonic acid and a hydrocarbon of more simple composition.

This law of the oxidation of organic substances, the truth of which appears to me to be quite independent of any theoretical speculations which may be formed respecting the constitution of organic atoms or of the organic acids, is alone capable of explaining facts which are opposed to all that we know, viz. that in processes of oxidation, products are obtained which contain less oxygen (frequently none at all) than the substance which has been oxidized;—it explains the origin of the hydrocarbons, of the organic oxides, of the aldehydes of a lower series, as well as the production of the carbonic acid which makes its appearance in these processes. These organic acids behave in this process of oxidation in an analogous manner to hippuric acid, leucine and glycocoll, the metamorphosis of which into benzamide, valeronitrile and prussic acid takes place according to a similar law*; nay, it is quite evident that it is also valid for the separations of higher organic atoms into compounds of a lower degree, quite independently of the causes which produce the separation. Thus, for instance, meconic acid is resolved into carbonic and comenic acids, comenic acid into carbonic and pyromeconic acids, acetic acid into carbonic acid and acetone. The difference between this and the other mode of separation is, that the whole of the oxygen which serves for the production of the eliminated carbonic acid is taken from the substance itself, and not from without. The appearance of carbonic acid in the fermentation of sugar, lactic acid and malic acid (in its metamorphosis into succinic and acetic acids), as well as that of hydrogen gas in the processes of fermentation, is based on the same law; the hydrogen gas is derived from the substance itself, or from the water which experiences decomposition, that is to say, it is set free owing to the oxygen combined with it being consumed in the formation of carbonic acid. I consider Kolbe's discovery to be a most important acquisition to science, because this law of oxidation is evidently the opposite to that of the formation of higher organic acids (containing little oxygen) from lower ones (containing much oxygen). The production

* If we subtract the elements of valeronitrile from those of leucine (the formula corrected according to Laurent, Gerhardt and Cahours)—

Leucine.....	$C^{12}\,N\,H^{13}\,O^4$
Valeronitrile.....	$C^{10}\,N\,H^9$
There remain ...	$C^2 \quad H^4\,O^4$

which, on the addition of 4 equivs. oxygen, are converted into water and carbonic acid. If we deduct 1 equiv. prussic acid from the elements of glycocoll—

Glycocoll	$C^4\,N\,H^5\,O^4$
Prussic acid	$C^2\,N\,H$
There likewise remains.....	$C^2 \quad H^4\,O^4$

of cholesterine, of oleic and margaric acids from starch or sugar, or from lactic acid or butyric acid, in the animal body, cannot be conceived except as an elimination of oxygen in the form of carbonic acid and of hydrogen in the form of water.—Liebig's *Annalen*, June 1849.

Cow's Milk containing Blood. By Prof. R. F. Marchand.

The author examined the milk of a cow, which several times after calving had yielded a milk resembling brown syrup more than the natural fluid. The animal exhibited no sign of disease. The author examined the first milk, and then fresh specimens every two days.

The first was of a blackish-brown colour, and even after standing for a considerable time did not yield a white scum. It was so tenacious, that it could hardly be made to flow from one vessel into the other. It had the odour of milk; was insipid, but like milk. Its specific gravity at 59° F. was 1·0922, whilst that of normal cow's milk is usually 1·02. On microscopic examination, a large number, but not the normal quantity, of milk-globules was perceived. In addition to these, it also contained a large number of well-developed granular corpuscles, which, as is well known, are peculiar to the colostrum. Numerous fibrinous bundles and flakes also existed in it, but no trace of blood-corpuscles could be detected. On analysis it was found that this milk contained the components of the blood in addition to all those of normal milk. When heated, it coagulated completely, like albumen, or rather like blood. The same occurred on the addition of spirit. This precipitate had exactly the appearance of that yielded by blood under the same circumstances. The alcoholic solution, which contained fat, was examined for sugar by the copper-test, and a large quantity was discovered. The precipitate produced by alcohol was digested with alcoholic sulphuric acid; it yielded a brownish-red clear solution, but was itself converted into a gray crumbly mass. The brown solution exhibited the well-known reactions of a similar solution of the red colouring matter of the blood. Brown flakes were precipitated by ammonia; these yielded a brownish-red powder, which, when dried and incinerated, gave about 9 per cent. of peroxide of iron. The milk yielded 29·24 per cent. of solid residue. This consisted of—

Fatty matter	1·75
Sugar	5·14
Caseine	2·20
Albumen	15·00
Fibrine	0·20
Hæmatine, &c.	4·95
	29·24
Water	70·76

The specimens which were subsequently examined gradually diminished in specific gravity, becoming at the same time clearer, yielding a creamy scum when set aside, and exhibiting fewer of the

fibrinous coagula and granular corpuscles; the amount of albumen simultaneously diminishing until the 24th day, when the liquid had acquired the characters of normal milk, except that it still contained a few granular cells. No blood-corpuscles could be detected throughout the course of this investigation, although the above facts showed that it contained blood.—*Journ. für Prakt. Chem.*, xlvii. p. 130–134.

On the Composition of the Bile of the Goose. *By* Th. Marsson.

The animals, the bile of which formed the subject of the present investigation, were fed upon oats. Immediately after its removal from the gall-bladders, the bile exerted a slightly acid reaction. It possessed a somewhat peculiar fatty odour, and a very intense dark green colour, and was of a somewhat thickish consistence. Still in no case could it be drawn into threads, although this might be done at a very low temperature. When treated with acetic or muriatic acid, a precipitate was immediately formed.

The average weight of the contents in eight gall-bladders was 3 grms.; the weight of the entire animal, including the feathers and blood, amounted on the average to 16 lbs.

Solid Constituents.—On drying the entire bile, in two separate instances, at 212° F., the results given under I. and II. were obtained; and on drying a portion of a mixture of the contents of eight gall-bladders at 266° F., the results given under III. were found:—

	I.	II.	III.
Solids.....	20·13	19·40	19·98
Water	79·87	80·60	80·02
	100·00	100·00	100·00

Inorganic Constituents.—The above specimens of bile, after having been dried in a platinum crucible, were incinerated. The ash was white, fused at a red heat, and effervesced with acids; the nitric solution yielded precipitates with nitrate of baryta and nitrate of silver, which were not soluble in excess of the acid; ammonia produced a gelatinous precipitate of phosphate of magnesia. It consisted essentially of carbonate and phosphate of soda, with some chloride of sodium and phosphate of magnesia. The ash of the three specimens of bile enumerated above amounted respectively to 2·04, 1·85 and 2·08 per cent. of the fresh undried bile.

Biliary Mucus.—When the bile was treated with 2 vols. of alcohol of 0·833 spec. grav. until any further precipitate ceased to be formed, it yielded on filtration a beautiful dark green solution; and the mucus, after having been washed on a weighed filter, first with dilute alcohol, and subsequently with alcohol of 0·833 spec. grav. until the latter passed through the filter in a colourless state, was of a dirty green colour, and amounted to 2·56 per cent. of the weight of the fresh bile.

Fatty Matter.—The bile which had been treated in the above

manner, on exhaustion with æther yielded the small amount of 0·36 per cent., of which cholesterine appeared to constitute a part; the æther at the same time acquired an acid reaction. Hence the proximate constituents of the bile of the goose are as follows:—

Fatty matter and cholesterine	0·36
Mucus	2·56
Pure bile and colouring matter	17·06
Water	80·02
	100·00

The Pure Bile (chenocholeate of soda).—The bile, when freed from the fatty matter and mucus, contains a remarkably large amount of colouring matter, which is difficult of separation. The alcoholic solution of the bile, when dried at 230° F., left, on re-solution in absolute alcohol, a somewhat considerable amount of a grayish-brown plastery mass, consisting of some bile and a large quantity of colouring matter. After the evaporation of the solution, the separation of the fatty matter from the residue by æther, and the re-solution of the latter in alcohol, the liquid could not be completely decolorized by treatment with good animal charcoal. On evaporation and desiccation at 212° F., the pure bile is obtained in the form of a readily pulverized mass, which yields a yellow powder. Its aqueous solution was strongly acid, tasted at first sweet and then strongly bitter, and differed essentially from the bile of the ox and pig in its behaviour towards reagents. Not the slightest precipitate was produced by either acetic acid, oxalic acid, nitrate of silver, acetate of lead or bichloride of mercury, even on the application of heat or after having been set aside for twenty-four hours. The fresh bile is precipitated by acetic acid; but this precipitation only arises from the mucus, after the separation of which no further precipitation occurs. Chloride of barium, chloride of calcium and muriatic acid immediately produce copious precipitates. These are white when first thrown down; but on agitating the vessel, they soon adhere in a plastery form to its walls. The barytic precipitate is dissolved by ebullition, even after the addition of ammonia; but again separates on cooling. Acetate of lead also causes a copious plastery precipitate, which is neither dissolved by excess of the precipitant nor on ebullition. The bile of the goose also yields the violet colour with sugar and sulphuric acid discovered by Pettenkofer.

On dissolving the pure bile in alcohol of 0·833 spec. grav. and adding hydrated æther, a precipitate is formed, which after a considerable lapse of time becomes converted into crystals, the formation of which is dependent upon the quantity of water existing in the liquids. When the solvents are concentrated, it remains plastery. The ash of the pure bile of the goose consisted principally of carbonate and sulphate of soda, with traces of sulphate of lime, phosphoric acid and chlorine.

The determinations of the sulphur in this bile show that it is one of those most abounding in this substance. Its deportment with the above-mentioned reagents, as also the crystallizability of the pure

bile, which is the soda salt of what is very probably a new acid, perhaps closely allied to the choleic acid of Strecker, justify us in distinguishing this acid provisionally from the other allied biliary acids by the name of *chenocholeic* acid. The purified bile, dried at 230° F., has, according to the author's analyses, the composition expressed under I. Hence the constituents of the organic matter combined with the soda are those detailed in II.:—

				I. Pure bile.	II. After deducting the NaO.
Carbon	..	..		57·19	60·06
Hydrogen	..	..		8·39	8·81
Nitrogen	..	..		3·48	3·66
Sulphur	6·45	6·23	mean	6·34	6·66
Oxygen	..	..		19·82	20·81
NaO	..	..		4·78	
				100·00	100·00
Ash	9·55	9·65	per cent.		

Archiv der Pharm., lviii. 138–148.

Observations on Valeramine or Valeric Ammonia. By A. Wurtz.

The cyanate of amylene, which I obtained by distilling sulphamylate of potash with cyanate of potash, is readily decomposed by a solution of potash. The reaction, assisted by heat, gives rise to carbonate of potash and a volatile base, valeramine, which distils over when the solution of potash is boiled. It is found in the receiver dissolved in the water which has been volatilized and condensed at the same time.

On saturating this solution of valeramine with hydrochloric acid, a perfectly neutral hydrochlorate is obtained, which may be procured in white spangles by evaporation. They are fatty to the touch, tolerably soluble in water and soluble in alcohol. The salt is not deliquescent. It furnished the following results on analysis:—

	Found.	Calculated.
Carbon	48·2	48·5
Hydrogen	11·4	11·3
Chlorine	28·3	28·7
Nitrogen	..	11·5

leading to the formula HCl, $C^{10} H^{13} N$. I have verified the accuracy of this formula by analysing the double salt which falls when concentrated solutions of the chloride of platinum and hydrochlorate of valeramine are mixed; as it is somewhat soluble in water, it is well to add a little alcohol to the mixture. After having collected and pressed the precipitate, it is dissolved in boiling water, from which it separates on cooling in the form of beautiful golden spangles. It furnished on analysis—

	Found.	Calculated.
Platinum	32·6	32·9
Chlorine	36·0	36·5
Carbon	20·4	20·5
Hydrogen		
Nitrogen	4·8	4·8

leading to the formula HCl, C^{10} H^{13} N, Pt Cl^2.

When the hydrochlorate of valeramine is distilled with lime, the volatile valeramine passes into the receiver. In the pure state this base is liquid, possesses a burning and bitter taste and a strongly ammoniacal odour. It is soluble in water; the solution precipitates salts of copper, but an excess of the reagent redissolves the precipitate, forming an azure-blue liquid. However, this solution of the hydrate of copper in valeramine is not effected so readily as in ethylamine, methylamine and ordinary ammonia. Valeramine likewise precipitates nitrate of silver; the precipitate is a fawn-coloured resinous mass, which adheres to the bottom of the vessel. An excess of the reagent whitens and entirely dissolves it.

Valeramine dissolves chloride of silver, but less readily than ammonia.—*Comptes Rendus*, August 13, 1849.

On the Sulphite of the Perchloride of Phosphorus.
By P. Kremers.

According to H. Rose, a combination of sulphuric acid with perchloride of phosphorus is obtained when sulphuric acid and protochloride of phosphorus are brought together, the latter being oxidized at the expense of the sulphuric acid. I have succeeded in preparing a similar compound by bringing together the same elements, only otherwise grouped. When, for instance, a current of dry sulphurous acid is passed over perchloride of phosphorus, these two substances combine, with considerable evolution of heat, into a greenish liquid. On rectifying it, a portion of the sulphurous acid escapes, and the distillate corresponds in composition to the formula $PCl^5, 2SO^2$*, and has the following per-centage composition:—

P = 11·73	The formula	$PCl^5, 2SO^2$	gives	11·71
Cl^5 = 64·24	...	...	...	64·87
S^2 = 12·23	...	...	...	11·71
O^4 = 11·80	...	...	...	11·71

This limpid, highly hygrometric compound, which is very troublesome to the eyes and organs of respiration, surpasses in refractive power the sulphuret of carbon, with which it has in common the property of dissolving iodine with a red colour. Its specific gravity at 57° F. was found to be 1·667; it boils at 212°. When poured into water, it sinks in drops to the bottom, like the sulphate of the perchloride of phosphorus, and is gradually decomposed into sulphurous, muriatic and phosphoric acids. No sulphuric acid is

* This compound has recently been prepared by Persoz.

formed on this occasion. This behaviour towards water was turned to account for its analysis, the sulphurous being converted by chlorate of potash into sulphuric acid. This compound dissolves a tolerable quantity of perchloride of phosphorus, which, on being set aside at the ordinary temperature, separates after some time in transparent square prisms, whilst according to H. Davy it crystallizes on fusion in columnar prisms. The mother-liquor from which the crystals had separated yielded on analysis results which also corresponded to the formula $PCl^5, 2SO^2$:—

P	= 12·12	The formula $PCl^5, 2SO^2$ gives			11·71
Cl^5	= 65·48	...	...	..	64·87
S^2	= 11·44	...	...	...	11·71
O^4	= 10·96	...	...	...	11·71

On comparing the last analysis with the first, it is found that the calculated formula is situated nearly between the two. In the first, the amount of sulphur and oxygen, in the second, that of the phosphorus and chlorine, is somewhat higher than required by theory; undoubtedly because in the first some sulphurous acid, and in the last some perchloride of phosphorus, is retained in solution; at least I found, after repeating the distillation, 0·4 per cent. less of sulphur in the first than the sample had previously yielded. Consequently to obtain this compound pure, it must be submitted to a second distillation. When sulphurous acid is passed through this compound, it absorbs another equivalent, which however is held in weak combination, and escapes even at the ordinary temperature, and still more readily at a gentle heat, which renders its analysis somewhat difficult. It furnished—

P	= 10·86	The formula $PCl^5, 3SO^2$ gives			10·48
Cl^5	= 59·07	...	...	...	58·08
S^3	= 15·88	...	...	...	15·72
O^6	= 14·19	...	...	...	15·72

It differs from the preceding by its lesser specific gravity and refractive power.

When ammonia is passed over the sulphite of the perchloride of phosphorus, the same phænomena are observed as when its constituents are treated separately with ammonia. There are obtained chloride of ammonium, dry bisulphite of ammonia, and a white powder, which does not differ from that obtained by treating perchloride of phosphorus with ammonia. A preliminary examination of the substance, dried at 212°, gave however only 36·18 per cent. phosphorus.—Liebig's *Annalen*, June 1849.

On the Fermentation of the Malate of Lime. *By* Prof. J. Liebig.

As it is probable that some chemists may have procured during the present season a supply of malate of lime for the preparation of succinic acid, it may be useful to add to the information previously

communicated some further experience respecting the fermentation of the malate of lime.

From the juice of the berries of the mountain ash, which had been neutralized with milk of lime and then mixed with beer-yeast, there separated, after ten days' standing at the ordinary temperature, colourless crystals of pure succinate of lime several lines in length; they were coated with a fine coloured powder, which consisted of carbonate of lime. I have observed, that the amount of succinic acid is greater the more slowly and quietly the fermentation is conducted. It is therefore of importance that the temperature during the fermentation, and the quantity of yeast or putrid cheese which is added, should not exceed a certain limit. 125 cub. centim. of yeast to 1 lb. of dry malate of lime and 6 lbs. of water proved to be a very good proportion. The disengagement of hydrogen is decidedly injurious; it indicates another process of fermentation, in which no succinic acid is formed, or that which has been formed is destroyed. In one case, in which 19 lbs. malate of lime were fermented with twice the usual quantity of cheese, on the seventh day the fermentation became so violent that the mass overflowed from the great disengagement of gas. Nearly the half of this gas proved to be hydrogen. In this experiment not more than 1 lb. of succinic acid was obtained from this large quantity of malate of lime.

The disappearance of the acetic acid in this experiment was remarkable; the mother-ley contained in its stead a quantity of butyric acid. From 24 to 30 oz. of oily butyric acid (which however was not free from acetic acid) were obtained from the mother-liquor. There is at the same time formed another volatile product, of an oily ætherial nature, which is procured by distilling the mother-liquor containing the lime salts; it is colourless, readily soluble in water, and has a powerful agreeable odour of apples. It is separated from water by carbonate of potash and by chloride of calcium (of which it dissolves a considerable quantity in the anhydrous state). It is one of the so-called fermentoles, of which several, as first suspected by Berzelius, are probably compounds similar to alcohol or the aldehydes.

The formation of the succinic acid is explained in the following manner:—6 equivs. malic acid take up the elements of 3 equivs. water, and produce 4 equivs. succinic acid, 4 equivs. carbonic acid and 1 equiv. acetic acid:—

$$\left.\begin{array}{l} 6 \text{ eq. malic acid} \ldots C^{24}H^{12}O^{24} \\ 3 \ldots \text{water} \ldots\ldots\ H^{3}O^{3} \end{array}\right\} = \left\{\begin{array}{l} 4 \text{ eq. succinic acid} \ldots C^{16}H^{12}O^{16} \\ 4 \ldots \text{carbonic acid} \ldots C^{4}\ \ O^{8} \\ 1 \ldots \text{acetic acid} \ldots\ldots C^{4}H^{3}O^{3} \end{array}\right.$$

If butyric acid is produced directly from malic acid, there should be disengaged on the whole, carbonic acid and hydrogen in the proportion by volume of 1 : 2; but as at least 3 equivs. of the carbonic acid are retained by the lime, the proportion of carbonic acid and hydrogen obtained should be as 10 : 8 or as 5 : 4 vols.

If we imagine butyric acid to be produced from succinic acid, the carbonic acid and hydrogen disengaged should be in the proportion of 2 : 1.

$$\left.\begin{array}{l} \text{4 equivs. malic acid..} \; C^{16}H^{8}O^{16} \\ \text{Add to which .....} \quad H^{4}O^{4} \end{array}\right\} = \begin{cases} C^{8}H^{8}O^{4}, \text{ butyric acid.} \\ H^{4} \\ C^{8} \quad O^{16} \end{cases}$$

$$C^{16}H^{12}O^{20} = C^{16}H^{12}O^{20}$$

Of the 8 equivs. carbonic acid, 3 are retained by the lime.

$$\text{3 equivs. succinic acid, } C^{12}H^{6}O^{12} = \begin{cases} C^{8}H^{8}O^{4}, \text{ butyric acid.} \\ H \\ C^{4} \quad O^{8} \end{cases}$$

Of the 4 equivs. carbonic acid, 2 equivs. are retained by the lime.

The following proportions of hydrogen and carbonic acid were obtained at different periods of the fermentation (accompanied by evolution of hydrogen):—

$$\begin{array}{l} 150\ H : 169\ CO^{2} = 4 : 4\frac{1}{2} \\ 140\ H : 140\ CO^{2} = 4 : 4 \\ 108\ H : 186\ CO^{2} = 4 : 7 \\ 120\ H : 220\ CO^{2} = 4 : 7\frac{1}{2} \\ 111\ H : 221\ CO^{2} = 4 : 8 \end{array}$$

From these relations it may be admitted that the butyric acid is produced both from the malic and the succinic acids, which would explain the decrease in the amount of the latter.

The following analyses of the products of this process of fermentation were made by Mr. Halerow.

The Acetate of Silver furnished—

Carbon.....	14·3	4 =	14·4
Hydrogen.....	1·9	3	1·8
Oxygen.....	..	3	14·3
Oxide of silver.....	69·3	1	69·5

The Butyric Acid gave—

Carbon.....	54·1	3 =	54·5
Hydrogen.....	9·2	3	9·1
Oxygen.....	..	4	36·4

Liebig's *Annalen*, June 1849.

Researches upon the artificial Production of some mineral and crystalline Substances, especially the Oxide of Tin, the Oxide of Titanium and Quartz. By M. A. Daubrée.

Production of the Oxides of Tin and Titanium and Silicic Acid in a crystalline form.—In a memoir which was submitted to the Academy in 1841, I showed that the fluorides appeared to have played a generating part in the formation of stanniferous deposits. That idea, which at the time was only based upon observations on the structure and the composition of the tin deposits, is now confirmed by experiment; for on imitating the natural process which I pointed out, I obtained the oxide of tin in a crystallized state. Except that,

instead of operating upon the fluoride, the preparation of which requires apparatus which is not at my disposal, I used the chloride. Moreover, the great analogy of the fluorides and chlorides allows us to extend the results obtained with the latter to the corresponding fluorides.

The process consists simply in conducting into a porcelain tube heated to redness two currents, one of perchloride of tin, the other of aqueous vapour. The stannic acid which results from the mutual decomposition of the two vapours is deposited in little crystals, which line the orifice of the porcelain tube. Larger crystals are obtained by using the perchloride of tin dissolved in a current of dry carbonic acid, instead of vaporizing the former substance by the mere action of heat.

The crystals of the oxide of tin, as thus obtained, are mostly colourless, possess the adamantine lustre peculiar to natural crystals, and are sufficiently hard to scratch glass with ease. Although very small, their facets and edges are perfectly distinct. They are right rhombic prisms, always very much flattened in one of the horizontal dimensions by two vertical facets of truncation. The bases of the primary prism do not exist, each of them being replaced by a pair of symmetrically placed facets (*biseaux*). The angles of the extreme summit of these crystals, the only ones which the minuteness of the facets permits to be measured by the reflecting goniometer, are respectively 133° and 89°. Being derived from the right rhombic prism, these crystals do not belong to the same crystalline system as those of the native oxide of tin, which belongs to the octohedron with a square base. Consequently the oxide of tin constitutes a new instance of dimorphism. These rhomboidal crystals of the oxide of tin present most resemblance in their crystalline system, their modifications and their physiognomy to those of Brookite, which is one of the three native forms of titanic acid. Like the crystals of Brookite, the crystals of the oxide of tin present longitudinal striæ parallel with the vertical angles of the primary prism. The similitude is completed by the angle of the two facets, which is 133° in the rhombic oxide of tin, corresponding to the angle (e^3 upon e^3) of Brookite, which, according to Levy, amounts to 134°. Hence the rhombic oxide of tin as obtained artificially is isomorphous with Brookite.

It has long been known that the native oxide of tin is isomorphous with rutile. The results which have been detailed teach us further, that the two primary forms of stannic acid correspond exactly with the two forms of titanic acid. This isodimorphism furnishes a new remarkable instance of the geometric relation which connects the two primary forms of a dimorphous substance. The specific gravity of the rhombic oxide of tin, which is 6·72, is inferior to that of the tetragonal oxide of tin. The same applies to the density of Brookite in comparison with that of rutile. In the two isodimorphous substances in question, the form of the square prism corresponds to a denser molecular aggregation than that of the right rhombic prism. Because the oxide of tin obtained by the action of the va-

pour of water upon the vapour of the perchloride of tin has not the same form as the natural oxide of tin, we ought not to conclude that these two systems of crystallization correspond to methods of generation which are very distinct from each other; for in Oisans and Switzerland the same veins, and sometimes the same specimens, contain at least two of the species of titanic acid, anatase and Brookite. Hence circumstances very intimately related to each other may give rise to the change of molecular equilibrium which the two forms of titanic acid exhibit.

The vapour of the perchloride of titanium, when treated by the same two processes as those to which the perchloride of tin was submitted, also furnishes titanic acid in little tubercles studded with perfectly distinct crystalline points, but the dimensions of which are microscopic. These minute crystals appear to have the same form as stannic acid when crystallized artificially, consequently as Brookite.

The chloride and the fluoride of silicium have been treated by the same processes. As the employment of the porcelain tube did not yield perfectly satisfactory results, I repeated the decomposition of the two vapours successively in an earthen retort and in a crucible, both of which were raised to a white heat. In two of these experiments I obtained with the chloride of silicium a deposit of silica with a vitreous fracture, the tuberculated surface of which presented here and there very minute crystalline facets, among which triangular facets similar to those of quartz were visible. The crystallization of quartz is much more difficult of accomplishment than that of titanic acid, and especially than that of the oxide of tin.

In the experiments which have been detailed, the porcelain tube was heated to a white heat; but the crystalline deposit of the stannic, titanic and silicic acids occurs at that end of the tube where the two vapours are conducted and in the part outside the furnace. The temperature of this portion of the tube did not exceed 590° F.—*Comptes Rendus, Aug.* 27, 1849.

ANALYTICAL CHEMISTRY.

On the Quantitative Determination of Antimony. *By* Prof. H. Rose.

Dilute solutions of antimony, in which the amount of metal is to be determined, must not be concentrated by evaporation when they contain muriatic acid, as is almost always the case, because perchloride of antimony escapes with the vapours of the muriatic acid, especially when the liquid is concentrated at too high a temperature. The volatilization of the antimony cannot be prevented by an addition of sulphuric acid, but it may be pretty nearly so by nitric acid.

When the antimony is precipitated from such solutions by sulphuretted hydrogen, the sulphur or the antimony has to be estimated in the precipitated sulphuret, which corresponds to the degree

of oxidation of the antimony. The author had previously stated that the reduction of the sulphuret of antimony is best effected in a porcelain crucible, into which hydrogen gas is conveyed by means of a porcelain tube. This process is far more easy of execution than the reduction in a bulb-tube.

The estimation of the sulphur in the sulphuret of antimony can be made in the usual manner, or by treating a weighed quantity of the sulphuret with muriatic acid. By this means only the perchloride of antimony ($SbCl^3$), corresponding in composition to antimonious acid, is formed, and the equivalent quantity of sulphur escapes in the form of sulphuretted hydrogen. The remainder of the sulphur separates in the solid form, which acquires, on long digestion with hot, highly concentrated muriatic acid, a pure yellow colour. It is collected on a weighed filter, washed first with water to which some muriatic and tartaric acid have been added, and finally with pure water. The weight of this sulphur indicates the amount of the sulphuret of antimony. According to this, the sulphosalts, which the highest sulphuret of antimony (SbS^5) forms with alkaline and other basic sulphurets, are treated directly with strong muriatic acid until the eliminated sulphur has a pure yellow colour, when it is weighed. But the antimony itself, as will be shown further on, can be estimated with perchloride of gold. In that case, however, the separated sulphur must be washed only with water and muriatic acid, and not with tartaric acid. 6·927 grms. of Schlippe's salt, $3NaS + SbS^5 + 18HO$, gave, according to this method, a residue of 0·449 grm. sulphur. According to theory, 0·455 ought to have been obtained. In another experiment, 10·049 grms. of Schlippe's salt gave 0·677 sulphur of a reddish colour, which left some sulphuret of antimony on combustion. Theory requires 0·660 grm. sulphur. This admixture of sulphuret of antimony can be avoided by the use of very strong muriatic acid.

Estimation of Antimonious Acid.—Antimonious acid (SbO^3) can be estimated in a similar manner to arsenious acid by means of a solution of the sodio- or ammonio-chloride of gold. The antimonious acid is dissolved in a very considerable excess of muriatic acid. After the liquids have been mixed, the whole is kept for several days in a gently heated place. When there is not a very large quantity of muriatic acid present, some antimonic acid separates with the reduced gold; and this, once eliminated, can only be dissolved with great difficulty by a very large amount of muriatic acid. After several days the reduced gold is collected on a filter; but the filtered liquid, containing the excess of perchloride of gold, is again set aside for some days, in order to see whether any further traces of gold separate. Some muriatic acid is added to the water used for washing. The reduced gold is ignited and weighed.

In case any antimonic acid has separated along with the reduced gold, it is removed by fusing the filter with its contents with nitrate and carbonate alkali, and the gold is weighed in the form of a regulus. Apparently borax cannot be used as a flux, as it furnished a red slag with loss of gold.

Separation of Antimony from Tin.—The author had previously described a method of separating these two metals, according to which the antimony was separated as antimoniate of soda by water from the solution of the tin in hydrate of soda. But since the antimoniate of soda is not perfectly insoluble in water, this method does not furnish very accurate results. It is better, when separating antimoniate of soda from stannate of soda, to use dilute alcohol precisely of the strength given below.

In the case of an alloy, it is reduced to as fine a state as possible, and treated in a large beaker with pure nitric acid of 1·4 spec. grav. The excess of acid is expelled and the oxide dried. It is heated to a faint red, and fused in a silver crucible with a considerable excess of pure hydrate of soda, and the mass kept for some time in a liquid state. The cold mass is moistened with water, the crucible completely cleansed with water, and the whole poured into a large beaker, in which the sparingly soluble antimoniate of soda is allowed to deposit. The stannate of soda, which contains the α-modification of the oxide of tin, remains entirely dissolved in the water. So much alcohol of 0·83 spec. grav. is now added to the aqueous liquid that the relative volume to that of the water used is as 1 to 3. The whole is well mixed, and set aside to deposit. The stannate of soda remains dissolved in the dilute alcohol, whilst the antimoniate of soda is completely separated. The carbonate of soda which had been formed during the fusion in the melting is likewise held in solution by the dilute alcohol, as well as the excess of hydrate of soda. The liquid is perfectly clear, and is easily filtered; the antimoniate of soda must then be washed with stronger spirit, consisting of equal volumes of water and alcohol of 0·83; and at last with still stronger spirit, consisting of 3 vols. alcohol of the above-mentioned strength, and 1 vol. water, until some of the filtered liquid, rendered acid with a little dilute sulphuric acid and mixed with a solution of sulphuretted hydrogen, no longer deposits, after long standing, any yellowish precipitate of sulphuret of tin. It is advisable to dissolve a very small quantity of carbonate of soda in the weak spirit used for the washing.

The alkaline liquid containing the stannate of soda in solution is now exposed to a gentle heat until the alcohol is expelled, diluted with water, supersaturated with sulphuric acid, precipitated with sulphuretted hydrogen, and the sulphuret of tin converted into oxide. The antimoniate of soda is treated in the manner described by the author in the separation of arsenic from antimony. On testing this method, M. Weber obtained—

	Used.	Found.
Antimony	57·85	58·86
Tin	42·15	40·04

The use of a silver crucible cannot be avoided. Sometimes, owing to this, the precipitated sulphuret of tin is contaminated with a very slight trace of black sulphuret of silver.

Separation of Antimony from Tin and Arsenic.—The metals are oxidized with very strong nitric acid, the oxidized mass evaporated to dryness, and then fused in a silver crucible with from 8 to 9 times the amount of hydrate of soda. The fused mass is mixed with a little water, and treated with dilute alcohol by adding to the aqueous liquid, alcohol of 0·83 spec. grav. until its volume becomes to that of the water as 1 : 3. The whole is set aside for twenty-four hours, frequently agitated, the precipitate collected on a filter, the glass rinsed with spirit, and the precipitate of antimoniate of soda washed as above directed for the separation of antimony from tin. The antimoniate of soda is dissolved in a mixture of muriatic and tartaric acids, from which solution the antimony is precipitated by sulphuretted hydrogen.

It is scarcely necessary to drive off the alcohol by heat from the liquid separated from the antimoniate of soda. It is supersaturated with muriatic acid, and sulphuretted hydrogen passed through it, without previously separating the precipitated arseniate of tin. The whole is set aside until it scarcely smells of sulphuretted hydrogen, and the precipitate collected on a weighed filter. The filtered liquid is heated for some time, by which any sulphuretted hydrogen still present and the greater portion of the alcohol are expelled. It is then mixed with a solution of sulphurous acid, and again treated with sulphuretted hydrogen, when generally a further small quantity of sulphuret of arsenic is precipitated. This treatment with sulphurous acid is however not necessary if sulphuretted hydrogen is again passed immediately through the liquid separated from the sulphurets. The small amount of sulphuret of arsenic which is precipitated in this case is always free from every trace of sulphuret of tin, and is kept separate, and only added to the sulphuret of arsenic obtained in the separation of the arsenic and tin. These two metals contained in the precipitate by sulphuretted hydrogen are separated by being heated in a current of sulphuretted hydrogen, when the sulphuret of arsenic is volatilized. The residual sulphuret of tin is converted into oxide, and the sublimed sulphuret of arsenic into arsenic acid. This method proved on examination to be absolutely accurate.

Separation of Antimonious Acid from Antimonic Acid.—These two acids may be quantitatively determined when they occur together in solution, by first determining in one portion of the solution the whole amount of antimony, and in the other the antimonious acid by means of perchloride of gold. This method however is limited in its application, for the solution must contain no nitric acid; the presence of muriatic or sulphuric acid is of no consequence. By means of the perchloride of gold the presence of any antimonious acid in antimonic acid can readily be detected, which is otherwise difficult. This applies especially to the combination of antimonic acid with oxide of antimony, SbO^3, SbO^5, which Berzelius formerly called antimonious acid, and which is left on calcining antimonic acid. To avoid any mistake, it may be as well to repeat here that at present the oxide SbO^3 is called oxide of antimony and

antimonious acid, according as it occurs as base or acid; and that the former antimonious acid, SbO^4, is regarded, even in the fifth edition of Berzelius, as antimoniate of the oxide of antimony $= SbO^3 + SbO^5$, and no longer as a distinct oxide.

Now heretofore it was not easy to detect the lower oxide of antimony in the compound insoluble in muriatic acid; but if it be fused in a silver crucible with hydrate of potash, the melted mass dissolves after cooling entirely in water. If it has not been fused too long, the alkaline solution, supersaturated with muriatic acid, reduces gold from a solution of the perchloride after some time, on the application of heat; whilst, when it has been fused too long with the hydrate of potash, the whole of the antimonious acid is oxidized into antimonic acid.

A solution of the nitrate of silver is a still more sensitive test for antimonious acid than the perchloride of gold. If, for instance, a solution of nitrate of silver is added to the solution of the antimoniate of the oxide of antimony, fused with hydrate of potash, a black precipitate is obtained, which is not soluble in ammonia, this dissolving only the precipitated oxide of silver and the antimoniate of silver. But when the antimoniate of the oxide of antimony has been kept fused for a considerable time with hydrate of potash, a black or brown precipitate is produced in the solution of the melted mass, which is entirely soluble in ammonia. This behaviour is explained from that of the different oxides. When, for instance, nitrate of silver is added to a solution of the antimonious acid in hydrate of potash, a deep black precipitate is obtained, which is not soluble in ammonia; but this removes oxide of silver from it, if any has been precipitated by the excess of potash. When ammonia is added first to a solution of antimonious acid in hydrate of potash (which produces no precipitate), and then nitrate of silver, only a slight black precipitate is obtained, which however increases with time. On the other hand, nitrate of silver causes in a solution of the antimoniate of potash a copious white, slightly yellowish precipitate of antimoniate of silver; and when the solution contains free potash, it is coloured brown by separated oxide of silver. Both precipitates are entirely soluble in ammonia. The smallest trace of antimonious acid which might occur in it is left as a black precipitate when the mass is treated with ammonia.

The perchloride of gold likewise produces in solutions of antimonious acid in potash a black precipitate, which is not further altered by being heated. When a solution of perchloride of gold is added to one of antimoniate of potash, no precipitate is produced, even though it contained free alkali, provided the potash was free from organic acids. A slight black precipitate is formed by long standing.

Lastly, antimonious acid can be distinguished from antimonic acid in a muriatic solution by oxalic acid. This so completely precipitates the antimonious acid, after long standing, if too much muriatic acid be not present, that the filtered liquid contains not a trace. The precipitate does not appear immediately with a large

addition of oxalic acid. From a solution of antimonic acid in muriatic acid, oxalic acid precipitates only a few flakes after long standing; tartaric acid prevents entirely, or nearly so, the precipitation of the antimonious acid by oxalic acid, as in the case of tartar-emetic. Perchloride of gold is very slowly reduced in the cold by tartar-emetic; the same is the case with a solution of silver. When the solution of tartar-emetic is mixed with potash, and then with nitrate of silver, a black precipitate, insoluble in ammonia, is formed.—Poggendorff's *Annalen*, lxxvii. p. 110.

PATENT.

Patent granted to James Castley *for Improvements in the Manufacture of Varnishes from Resinous Substances.*

The first part of this invention consists in manufacturing a strongly adhesive and perfectly water-repellent varnish from resin spirit and gutta percha.

3 parts by weight of the gutta percha of commerce are put into a pot with 9 parts of crude resin spirit (obtained by the destructive distillation of common resin), and subjected to a heat of from 120° to 140° F., the mixture being stirred occasionally until the gutta percha is dissolved. The varnish thus produced is suitable for coating coarse fabrics, such as tarpaulins, rick-cloths, &c.; but to obtain a varnish suitable for fine articles, the patentee substitutes for the crude resin spirit above-mentioned a rectified resin spirit, obtained by passing a current of steam through the crude resin spirit until the condensed product which comes over attains a specific gravity of about 0·870; at which point the process of distillation must be stopped, as all products of a higher specific gravity will be injurious to the quality of the spirit.

The second part of this invention consists in manufacturing a colourless varnish from resin spirit and gum damar, or from resin spirit and gum mastic.

The patentee mixes resin spirit, which has been rectified by steam in the manner above described, with from one-tenth to one-sixth of its weight of sulphuric acid of not less than 1·700 spec. grav., and thoroughly agitates the mixture; then he rectifies the spirit again by a current of steam, when the spirit comes over in a colourless state; after which he dissolves the gum damar or gum mastic in about four times its weight of this purified rectified spirit, with the aid of a gentle heat. An inferior varnish may be obtained by using resin spirit which has undergone only one process of rectification and has not been treated with sulphuric acid.—Sealed Jan. 11, 1849.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Nitrogenous Constituents of Vegetables as the Sources of artificial Alkaloids. By Dr. J. Stenhouse.

There are few branches of organic chemistry which during the last six or seven years have attracted more attention than the artificial preparation of alkaloids. This is not to be wondered at if we bear in mind the interest which this class of bodies presents both with respect to their definite chemical properties as well as to the medicinal virtue some of them possess. All experiments to prepare artificially such alkaloids as quinine, cinchonine, &c., have hitherto proved unsuccessful; whilst, on the other hand, the chemist has actually succeeded in preparing by various processes a considerable number of true alkaloids perfectly analogous to those which occur in nature. Several of these artificial alkaloids, as quinoline, narcogenine, cotarnine, &c., are obtained from the natural alkaloids by treating them with certain reagents. A second group, to which furfurine, thiosinnamine, &c. belong, is obtained on bringing together ammonia and some of the essential oils, for instance oil of mustard. A third and very numerous group, containing nitraniline, toluidine, cumidine, &c., is produced by the reducing action of sulphuretted hydrogen or sulphuret of ammonium upon nitrogenous compounds, obtained by treating certain hydrocarbons with nitric acid. A fourth and very important group contains aniline, picoline, petinine, &c., which are obtained in the distillation of fossil coal or of animal substances, as in the preparation of bone-oil and animal charcoal. It is especially to this last group that this notice refers.

It is somewhat surprising, that, after the discovery of so many other sources for these alkaloids, hitherto, as far as I am aware, no attempt has been made to procure them from the highly nitrogenous principles which occur in all plants, frequently in very considerable quantity, under the name of vegetable albumen, fibrine, caseine, &c. These constituents contain nearly as much nitrogen as the corresponding animal compounds, on an average about 15 per cent. The neglect of these substances by chemists is the more remarkable, considering that of the known sources for the artificial alkaloids, fossil coal has proved one of the most productive, and has furnished besides ammonia four other bases, viz. quinoline, aniline, picoline and pyrrole,

whilst it probably contains several others which have hitherto escaped observation. Now fossil coal is, according to the general opinion, exclusively of vegetable origin, consisting of the remains of various plants, which in the state of putrid fermentation under an exceedingly great pressure have laid buried in the earth since time immemorial. On thinking over the probable sources of the organic bases in coal, it appeared to me evident that they could not owe their origin to the woody fibre and the other non-nitrogenous vegetable principles of which coal is principally constituted, but that they were derived from the above-mentioned nitrogenous principles which were contained in the plants of the coal formation. We have therefore every reason to suppose that, by acting on the nitrogenous constituents of recent plants, the same organic bases, or at all events a series of analogous bases, would be obtained in proportionately greater quantity. It will be seen from the following that the latter expectation has not been disappointed. It is difficult to obtain pure vegetable albumen, fibrine or caseine in any quantity; instead therefore of attempting to purify these substances, I contented myself with selecting those parts of the plants, principally the seeds, which contained the greatest amount of those principles. I made the first experiment with the common bean (*Phaseolus communis*). They contain 20·8 per cent. of caseine and 1·35 albumen. The beans were submitted to dry distillation in cast-iron cylinders of about 3 feet high and 8 inches in diameter. The products were condensed by means of a large Liebig's refrigerator. A considerable quantity of a combustible non-condensable gas, of extremely disagreeable odour, was disengaged. The liquid which passed over was strongly alkaline, requiring about a third of ordinary muriatic acid to saturate it. The distillate resembled in every respect the products resulting from the distillation of bones, flesh and other animal substances, and contained acetone, pyroligneous spirit, acetic acid, empyreumatic oils, tar, a very large amount of ammonia and several organic bases. The crude product was treated with a considerable excess of muriatic acid, and the clear liquid decanted after the tar had subsided. The tarry residue was several times exhausted with water containing muriatic acid, and the various extracts mixed and boiled for several hours in a copper pan or in an enamelled iron pan. By this means, acetone, pyroxylic spirit, and a great portion of the neutral and acid empyreumatic oils, are volatilized or separated by resinification. The acid liquid was, after cooling, filtered through pounded wood charcoal, which retained most of the resinous matter, and then supersaturated with lime or soda in a large still, and submitted to distillation. When the liquid began to boil, a large amount of ammonia was disengaged; a quantity of oily bases appeared on the surface of the ammoniacal liquid, which increased in the course of the distillation. As the first portion of the liquid which passed over was richest, it was collected separately; what followed consisted principally of an aqueous solution of the bases, and contained but little separated oil. The distillation was continued as long as the product had an alkaline reaction. The oily mixture

which had collected on the surface of the first portion was removed with a pipette and dissolved in muriatic acid, when the neutral oil it contained was left undissolved, and could be separated by filtration through a moistened filter. The solution was supersaturated with carbonate of soda, and rectified in a large glass retort. It was found advantageous to employ a great excess of alkali, as these bases are far more soluble in water than in alkaline liquids; and therefore distil over more readily when separated by the alkali. The basic oils collected in the receiver were separated as above with a pipette from the ammoniacal liquid, and preserved in suitable bottles. The slightly alkaline liquids of the preceding distillation, from which no longer any oil separated, were again saturated with muriatic acid, and concentrated by evaporation at a gentle heat. By boiling these liquids too long, there is always a considerable loss of alkaloid, a portion of which becomes oxidized, and separates as a dark resin. The basic oils were rectified repeatedly with water, when more resinous matter was separated. To free them from still adherent ammonia, they were repeatedly agitated with strong solution of caustic potash, and separated from the ammoniacal potash ley by means of a funnel. This operation, which was continued until the oils were perfectly free from ammonia, is accompanied by an unavoidable loss. The next step was to free the bases from the dissolved water, of which they contained nearly half their volume. This was effected by leaving them in contact for several days with fused caustic potash, and frequently agitating the mixture. To be certain of having removed the whole of the water, they were mixed with fresh quantities of dry potash until the latter was no longer moistened after long standing. The clear liquid was now decanted, and carefully rectified. The first two-thirds which distilled over consisted of a colourless transparent oil. The last portions, which came over at a higher temperature, were coloured slightly yellow, especially towards the close of the distillation. The colourless and coloured distillates were therefore kept separate; however, the latter were obtained perfectly colourless by repeated rectifications. As the considerable variation in the boiling-point showed distinctly that the substance in question was a mixture of bases, various experiments were made to separate them by fractionated distillation. At 226° F. the liquid began to boil, and a very small quantity of a transparent colourless oil distilled over, which was collected separately. The thermometer now rapidly rose to 248°, and from that up to 266°; at both which points small portions were collected. The boiling-point remained constant for a considerable time between 302° and 311°, and a large quantity of oil distilled over; about an equal amount was collected between 320° and 329°. The boiling-points of the last portions which passed over were between 329° and 428°. The products of these different distillations were again rectified, and in this manner oils obtained, the boiling-points of which corresponded more closely with those at which the thermometer remained longest stationary in the first distillations.

Although these different bases varied so considerably in their

boiling-points, they were very similar in other respects. They are colourless transparent oils, of strong refractive power, lighter than water, and possess the peculiar, pungent, slightly aromatic odour characteristic of this class of compounds. The odour adheres to the hands and clothes for a very long time, and is strongest and most pungent in the more volatile bases; they have a hot taste, which is not disagreeable in the dilute state, and resembles oil of peppermint. The bases which distilled over at a lower temperature are tolerably soluble in water, and decidedly more soluble than those with higher boiling-points. They all dissolve in every proportion in alcohol and æther, and exhibit a very powerful alkaline reaction upon curcuma and reddened litmus-paper. A glass rod, moistened with muriatic acid and held over them, produced copious white fumes. They neutralize acids completely, and form in general crystalline salts, and likewise crystalline double salts with the chlorides of platinum, gold and mercury, which are about as soluble in water as the corresponding ammonia compounds. Some of the platina salts crystallize in beautiful four-sided prisms. The salts of the bases with higher boiling-points were however frequently contaminated with a brown resin, and could not be obtained well crystallized; the same was the case with the salts of gold. They precipitate, like ammonia, salts of iron and copper; and the precipitates of the latter dissolve in an excess with a beautiful blue colour. They were kept in closed bottles, which however were opened pretty frequently, but nevertheless remained transparent and colourless. When, however, they are exposed for some time to the light, the bases with higher boiling-points acquire a deep yellow colour. The bases are readily oxidized. When treated with nitric acid, they are quickly converted into yellow resins, without however nitropicric acid being produced. With chloride of lime they are converted into brown resins, without a trace of aniline being detectable. When the bases were boiled in a retort for a few minutes, they gradually became coloured, although what distilled over was as colourless as before. When the distillation was terminated, a small quantity of dark brown resin was left in the retort.

I will now add a few very imperfect details, in order to give an idea of the nature of these bases. I regret that the difficulties I have hitherto met with in procuring larger quantities have prevented me from submitting them to such an accurate examination as they deserve. I hope however to be able to accomplish this sooner or later.

The base, which distilled over between 302° and 311°, furnished—

Carbon.....	74·60	74·78	10 =	740·0	74·98
Hydrogen.....	8·18	7·77	6	75·0	7·49
Nitrogen	..	..	1	175·2	17·53

On mixing the anhydrous base with muriatic acid, considerable heat was evolved. The muriatic compound was very soluble in water, and crystallized on evaporation in transparent prisms. It formed similar crystalline salts with sulphuric and nitric acids. The plati-

num salt was readily soluble in minute four-sided prisms of an intense yellow colour. It was somewhat less soluble in water than the corresponding ammonia compound. It was purified by repeated crystallization from water, by which it was freed from a small quantity of a resinous matter. It furnished 34·72 and 34·60 per cent. platinum; the formula $C^{10}H^6N, HCl, PtCl^2$ requires 34·50.

A double salt was immediately formed on mixing chloride of gold with a muriatic solution of this base. It crystallized in beautiful light yellow needles, which dissolve very readily in hot water, and again separate on cooling.

It is readily seen that this base, the probable formula of which is $C^{10}H^6N$, approaches very closely in its composition to nicotine, and in its properties to picoline, the base discovered by Dr. Anderson in coal-tar. The formula of nicotine is $C^{10}H^8N$. The boiling-point of the new base is higher than that of picoline, and its solubility in water much less. Dr. Anderson observes respecting picoline, that it dissolves in every proportion in water; the new base requires at least from 6 to 7 parts of water for solution. It is lighter than water; the odour is peculiar and slightly aromatic; the taste burning and somewhat like oil of peppermint. It keeps perfectly colourless in closed vessels not exposed to light. When heated, it quickly takes fire, and burns with a bright smoky flame.

To obtain an approximate idea of the per-centage composition of the other bases which accompanied the preceding one, three of the different distillates were submitted to analysis. I. is a substance which boiled between 320° and 329°; II. is a substance which boiled between 329° and 338°; and III. is a substance which boiled between 392° and 410°:—

	I.	II.	III.
Carbon	74·08	75·42	75·63
Hydrogen	8·06	8·52	8·73

It is remarkable that the amount of carbon and hydrogen does not vary more, whilst the boiling-points of these bases (or basic mixtures) are so far apart. They all form double salts with chloride of platinum and gold. However, those with higher boiling-points are usually contaminated with more or less resin. They all appear to possess equally strong basic properties.

I selected for a second experiment the seed of *Linum usitatissimum*, or rather the expressed oil-cake, as a type of that class of plants in which the starch which the *Gramineæ* contain is replaced by oil, as for instance in *Papaver somniferum*, *Brassica Rapa*, *Sinapis*, &c. They all contain very large quantities of albumen. The oil-cakes were broken into small fragments, and subjected to distillation in the previously-mentioned cylinders. The quantity operated upon was rather more than 2 cwts. The oil-cakes yielded, as was to be expected, comparatively much less liquid products than the beans. The odour was peculiarly disagreeable. The distillate consisted of acetone, acetic acid, and a large amount of tar and empyreumatic oils. The quantity of ammonia was likewise very considerable; but unfortunately the amount of organic bases was much

less than I had expected, and perhaps scarcely a third of that I had obtained from the beans. This may perhaps be ascribed to the much higher temperature required for distilling the oil-cake; as, from its containing less water, the heat was raised higher than in the case of the beans. Now since all these volatile alkaloids experience decomposition at a high temperature, with disengagement of ammonia, I think I am justified in assuming that in this, and in many other cases, a large portion of the bases which would have been produced at a lower temperature are either not formed or immediately destroyed after their production. The large amount of ammonia and the small quantity of organic bases may be explained in this manner.

The bases obtained from the oil-cake were separated and purified in the same manner as stated in reference to the bases from the beans. They also consisted of a mixture of basic oils, distinct from those obtained from fossil coal or bones, as they contained neither aniline nor quinoline. They likewise differed in their odour from those obtained from beans, which in other respects they very much resembled. Their basic properties are quite as decided, and they form similar salts. It is therefore highly probable that some of the bases of these two series are identical.

Wheat.—The product resulting from the distillation of wheat-flour was different from the two others and very strongly acid, arising from the large quantity of acetic acid produced from the considerable amount of starch in the seed. Acetone and pyroxylic spirit are likewise present in considerable quantity. The empyreumatic oils were of a less disagreeable odour than those of the preceding distillations; there was a pretty considerable amount of ammonia present, but the quantity of organic bases was small beyond expectation. They contained neither aniline nor quinoline, and appeared in their general properties to be quite similar to the preceding series; they however appeared to be of more volatile nature, as they distilled over at a far lower temperature.

Turf.—The material operated upon was from the neighbourhood of Glasgow; the products of the distillation were nearly neutral, owing to the large amount of acetic acid. There was, moreover, much acetone and pyroxylic spirit. The crude distillate was supersaturated with muriatic acid, and boiled to expel acetone and pyroxylic spirit, which held in solution a portion of the tar. Upon cooling, the tar separated on the surface as a semisolid crust, and was easily removed. The clear liquid was then saturated with carbonate of soda and distilled. The ammoniacal liquid which came over contained a considerable amount of organic bases, which floated on the surface in the form of an oil. These were freed from ammonia, and purified as above described. I hoped to find aniline in this mixture; but it appears to contain neither aniline nor quinoline. They bore great resemblance to those of the preceding series; but whether they are identical with them or not I am at present unable to tell.

Wood.—I was enabled to examine, through the kindness of Mr.

Turnbull, considerable quantities of the crude products of distillation of beech, oak, ash, and other hard woods. The stems and thicker branches of the trees were exclusively used. I was much astonished to find that these liquids contained scarcely a trace of ammonia and of other organic bases. It appears therefore that the stems of trees are almost perfectly free from nitrogenous matter, in which respect they form a remarkable contrast to turf; a circumstance which appears to me capable of throwing some light upon a very interesting question, the origin of fossil-coal.

[To be continued.]

On a Copper Amalgam. By Dr. Max Pettenkofer.

In Paris some dentists employ an amalgam of copper with great advantage for filling the cavities of carious teeth. This amalgam is sold in little cakes, which weigh between 4 and 5 grms. and cost two francs each. The surface is of a grayish colour; the hardness is very considerable, and the adhesion of the minutest parts so strong, that the amalgam requires a powerful stroke of the hammer to be broken. It has a finely granular crystalline texture. A sample examined by me consisted of 30 parts of copper and 70 parts of mercury. When this amalgam is heated nearly to the boiling-point of mercury, it has the peculiarity of swelling somewhat, and a few drops of mercury appear on the surface. When it is now triturated for some length of time in a mortar, it becomes after cooling so soft that it may be kneaded between the fingers like moist clay. In this state it can be pressed into the smallest cavities. After a few hours it becomes so hard, that with a sharp-edged piece of this copper amalgam one can engrave upon tin and cut bone. When the previously-hardened amalgam is again warmed, and submitted to the above-mentioned manipulations, it again becomes plastic, and after a few hours again solidifies. In the soft state, a very liquid amalgam of copper and mercury can be expressed by a powerful pressure between the fingers. The specific gravity of the plastic copper amalgam in the soft and hard state appears to differ very little.

This metallic compound is a very interesting example of the effects of crystallization and amorphism on the properties of bodies. In the soft state it shows not a trace of crystallization. It can be spread on an anvil with a knife or hammer, like plaster; but when hardened it is very brittle; thin layers break like glass, and the fracture is granular crystalline. Among the metals this copper amalgam is the first known example of the two states of a body at the same temperature; and it is quite as instructive as the elastic amorphous sulphur and the brittle stick-sulphur is amongst the metalloids. That the specific gravity of the amalgam does not vary perceptibly in the transition from the amorphous into the crystalline state, is for the purposes of the dentist a most valuable property, as it must be of importance that the mass after cooling should occupy exactly the same space as in the soft state. I have pressed the plastic amalgam

into glass tubes, and let it harden in them; after cooling, it formed a perfectly air-tight stopper.

I have prepared amalgams which contained between 25 and 33 per cent. of copper, and all solidified to a crystalline mass after being heated; those which contained most copper solidified more quickly and became much harder than those containing less. Alloys of 25 parts copper with 75 parts mercury required three days to pass completely into the crystalline state. There is no atomic proportion between the copper and mercury in these crystalline compounds, any more than between the constituents of other metallic alloys. Were we to suppose a combination of 1 equiv. copper with 1 equiv. mercury, this would require in 100 parts, 23·8 copper and 76·2 mercury. Perfectly analogous compounds occur in the native crystalline silver amalgams; the analyses have shown their amount of silver to vary between 25 and 86 per cent. When therefore two metals can crystallize together, this merely proves that they are isomorphous. This is the case with copper, silver, gold and mercury.

This copper amalgam is likewise interesting as an example of the transference of the state of aggregation from one body to another; the liquid mercury passes with the solid copper into the same firm crystalline state, which alone it is only capable of assuming at a very low temperature, as many salts pass from the solid into the liquid state by contact with water.

The preparation of the copper amalgam does not succeed according to every method. I had to try several plans before I obtained it equal to the Paris sample. I found the following to be the best:—A weighed quantity of mercury is dissolved in boiling sulphuric acid, and the crystalline paste of the sulphate of the per- and protoxide of mercury, triturated with finely-divided metallic copper in a mortar with water, at 140° to 158° F., for some length of time. There must be so much metallic copper present, that in the first place the whole of the mercury is reduced; and secondly, that as much copper can amalgamate with the reduced mercury as the alloy requires. The copper obtained by reducing oxide in hydrogen is best suited for the purpose; but that precipitated by iron from sulphate of copper is likewise applicable. The well-washed plastic amalgam is placed in a leather bag, and as much mercury as possible pressed out of it; it is then formed into little cakes; after several hours, varying with the amount of mercury, it hardens to a mass, the fracture of which resembles in appearance the brittle alloy of gold and lead. The first hardening requires much more time than the second; when, for instance, it is made soft for use, it sets much quicker.

The useful applications of this amalgam are evident from its physical and chemical properties; for instance, for stopping machines and chemical apparatus where cork, glass, caoutchouc, cement, &c., cannot well be used; and there may likewise be cases where it will prove of service to the artist and the surgeon.

[In an editorial note it is stated that this copper amalgam may be very easily procured by moistening finely-divided copper, precipi-

tated from a solution of the sulphate of iron, with protonitrate of mercury, in a porcelain mortar, pouring boiling water over it with the addition of metallic mercury, and triturating it uninterruptedly for some time. At first the mass is brittle, but soon becomes soft, and acquires, when the right quantity of mercury has been incorporated, the desired salve-like consistence.]—*Ann. der Chem. und Pharm.*, June 1849.

On the Products of Decomposition of Aloes by Nitric Acid. *By* Prof. Mulder.

[Continued from p. 362.]

Chrysammate of Baryta and Chrysammide-baryta, $BaO,C^{14}HN^2O^{11} + BaO, C^{14} H^3 N^3 O^{10}$.—This double salt is formed when chrysammic acid mixed with ammonia is set aside until the whole is converted into chrysammide; chloride of barium is then added, and the precipitated chrysammide-baryta is dried in the air. At 212° it parts with ammonia; at 248° it becomes anhydrous, but with further loss of ammonia. In the air-dried state the precipitate should have the composition $BaO, C^{14} H^3 N^3 O^{11} + n HO$. When perfectly dry it corresponds in composition to the formula above given, as is evident from the following analysis by Vlaanderen:—

Carbon	30·1	..	28	29·9
Hydrogen	1·5	..	4	0·7
Nitrogen	12·4	12·1	5	12·4
Oxygen	27·6	..	21	29·8
Baryta	28·4	..	2	27·2

The name amido-chrysammic acid, applied to it by Schunck, is consequently no longer suited. Chrysammide is converted by heat and muriatic acid into more or less green chrysammic acid. From his description of it as being *dark olive-green*, it would appear that his product was nearly pure chrysammic acid with very little chrysammide. His analysis of the amido-chrysammate of baryta likewise agrees pretty accurately with the composition of chrysammate of baryta with 2 equivs. of water, as follows:—

	Schunck.		
Carbon	29·93	14	28·5
Hydrogen	1·77	3	1·0
Nitrogen	..	2	9·5
Oxygen	..	13	35·1
Baryta	25·11	1	25·9

Aloe-resinic Acid (Mulder), $C^{14} H^3 N O^{12} + HO$.—Mulder has applied this name to the acid contained in the brown liquid which remains after the treatment of aloes with nitric acid, and separating the two acids previously described. Schunck, in his first memoir, has assigned to it the name aloe-resinic acid, but a different composition; and in his last paper has considered as identical with it a product of

decomposition of chrysammic acid, which however is distinct, and which Mulder calls chrysatric acid.

The brown liquid resulting from the action of the nitric acid upon aloes contains, moreover, the whole excess of nitric acid and oxalic acid. It is saturated with chalk, and the filtered neutral solution precipitated with acetate of lead. The precipitate does not exhibit a constant amount of oxide of lead; but the organic substance combined with it has always the same composition provided the directions given for the preparation of the aloetic acid are accurately followed. The lead salt, suspended in water and decomposed with sulphuretted hydrogen, furnishes on evaporation a brown amorphous mass. Vlaanderen found the following results in the analyses of the lead salts, dried at 266°, for the organic substance contained in them:—

	I.		II.			
Carbon	42·7	42·8	42·3	14	= 1051·68	42·7
Hydrogen	2·2	1·9	2·4	3	37·44	1·5
Nitrogen	7·4	7·4	7·4	1	175·00	7·1
Oxygen	47·7	47·9	47·9	12	1200·00	48·7

In I. the salt contained 61·8, in II. 58·4 per cent. oxide of lead. The first quantity corresponds to the formula $C^{14} H^3 NO^{12} + 3PbO$, and requires 63·0 per cent.; the second quantity corresponds to the formula $2(C^{14} H^3 N O^{12}) + 5PbO$, which requires 58·6 per cent. This last salt can be separated, by treatment with hot water, into the first of the preceding salts, and into a second soluble salt, which is obtained on evaporation, of the composition $C^{14} H^3 N O^{12} + 2PbO$. According to what has been stated above, the three acids produced by the action of nitric acid upon aloes stand in their free state in the following relation to each other:—

	Hydrated acid.	Deducting HO.
Chrysammic acid..	$C^{14} H N^2 O^{11} + HO$	$C^{14} H N^2 O^{10} + O$
Aloetic acid	$C^{14} H^2 N^2 O^{10} + HO$	$C^{14} H N^2 O^{10} + H$
Aloe-resinic acid ..	$C^{14} H^3 N O^{12} + HO$	$C^{14} H^2 N O^{10} + O$

whence their behaviour towards oxidizing and reducing agents is evident. Aloe-resinic acid furnishes with lime, soda, potash and baryta, brown uncrystallizable soluble salts; with lead, copper and silver, brown insoluble salts. They yield on boiling with concentrated nitric acid aloetic acid, which is then converted into chrysammic acid. Aloe-resinic acid is consequently the primitive product of the action of nitric acid upon aloes, which by the exchange of H, N, O is converted into the others:—

Aloe-resinic acid $= C^{14} H^3 N O^{12}$, aloetic acid $= C^{14} H^2 N^2 O^{10}$;

and that is the reason why chrysammic acid, which has not been treated sufficiently long with nitric acid, is contaminated with aloe-resinic acid, which colours it brown, and with aloetic acid, which imparts to it an orange colour. Thus Boutin's *polychromatic acid* is a chrysammic acid contaminated with aloetic and aloe-resinic acids.

Chrysatric Acid, $C^{24}H^6N^3O^{15}$ (as contained in the lead salt dried at 266°).—This acid is formed from chrysammic or aloetic acids when they are heated with solutions of the fixed alkalies and alkaline earths. It is similar to the preceding ones in several respects, but decidedly distinct. Chrysammic acid is rapidly dissolved by potash into a brown liquid, in which acetic acid produces no precipitate, but disengages carbonic and formic acids. With concentrated solution of potash the carbonic acid is in greatest proportion, while with a weak solution the formic acid preponderates. During the reaction, concentrated solution of potash expels ammonia, and acids then disengage prussic acid from the liquid, which contains nitric acid. A weak solution of potash does not liberate any ammonia.

Chrysatric acid, or rather a constant lead salt of it, is obtained when chrysammic acid is warmed with an excess of moderately concentrated solution of caustic potash, and then heated to boiling. As soon as the whole is dissolved to a homogeneous brown liquid, it is diluted with water, filtered, and heated with an excess of acetic acid; no precipitate is formed; after cooling, it is mixed with acetate of lead. The brown precipitate, washed and dried at 266°, is chrysatrate of lead, in which Rost van Tonningen found 58·64 and 58·78 per cent. oxide of lead, and for the organic acid combined with it—

Carbon	46·22	46·15	24 =	1802·88	46·2
Hydrogen	1·89	1·89	6	74·88	1·9
Nitrogen.....	13·01	13·69	3	525·00	13·5
Oxygen	38·88	38·27	15	1500·00	38·4

The lead salt of chrysatric acid which served for the preceding analyses must, from the amount of the oxide of lead, have the formula $4PbO + C^{24}H^6N^3O^{15}$. Chrysatric acid may be produced in the following manner from chrysammic acid:—

$$2(C^{14}H^2N^2O^{12}) + 3HO = C^{24}H^6N^3O^{15} + C^2HO^3 + C^2O^4 + NO^5.$$

This expression must be altered when strong caustic potash is used, as ammonia and prussic acid then occur among the products. Chrysatric acid dissolves in water and dilute acids; its salts, with the alkalies and alkaline earths, are soluble; its lead and silver salt insoluble. It is sufficiently distinguished from aloetic acid by its not being reconverted into chrysammic acid on treatment with nitric acid.

The composition of this acid throws further light on the constitution of chrysammic acid. On a former occasion Mulder observed that chrysammide behaved like a conjugate oxamide, and that chrysammic acid very probably contained oxalic acid. We have—

$$\left.\begin{array}{ll} \text{Chrysammide.... } & C^{14}H^4N^3O^{11} - C^2H^2NO \\ \text{Chrysammic acid } & C^{14}H^2N^2O^{12} - C^2O^3 \end{array}\right\} = C^{12}H^2N^2O^9.$$

If we subtract from this residue NO^5, there remains $C^{12}H^2NO^4$, *i. e.* the same group which nitro-picric acid leaves after deduction of $NO^5 + NO^4$—

$$\text{Picric acid, } C^{12}H^2N^3O^{13} - N^2O^9 = C^{12}H^2NO^4.$$

This same group again occurs in chrysatric acid—

$$C^{24}H^6N^3O^{15} - NO^5\,2HO = 2(C^{12}H^3NO^4).$$

The chrysatric acid was formed from chrysammic acid by the separation of NO^5, $HO + 2C^2O^3$, and by the assimilation of 3HO. It therefore really appears that chrysammic acid consists of $C^{12}H^2NO^4$ with 1 atom of oxalic acid + 1 atom nitric acid. We have further—

Indigotic acid .. $C^{14}H^4N\,O^7 = C^{12}H^2NO^4 + C^2O^3 + 2HO$
Styphnic acid .. $C^{12}H^2N^3O^{15} = C^{12}H^2NO^4 + O + 2NO^5$
Chrysatric acid .. $C^{24}H^6N^3O^{15} = 2(C^{12}H^3NO^4) + NO^5 + 2HO$

Finally, the following simple expression, which was first discussed by Marchand in his paper on nitro-picric acid, and which has since been further confirmed by Hoffmann's researches on aniline, may be given to this series. If, for instance, we admit the conjunct $C^{12}H^4$ in aniline, the conjunct in the picric acid series is $C^{12}H$; and the following substances then stand as follows:—

Nitro-picric acid..... = $C^{12}H + 3NO^4, HO$
Styphnic acid ..... = $C^{12}H + 2NO^5 + NO^4 + HO$
Anilic acid ..... = $C^{12}H + NO^3 + C^2O^3 + 3HO$
Chrysammic acid .... = $C^{12}H + 2NO^4 + C^2O^3$
Aloetic acid..... = $C^{12}H + 2NO^3 + C^2O^3 + HO$
Aloe-resinic acid..... = $C^{12}H + NO^5 + C^2O^3 + 2HO + O^2$
Chrysatric acid ..... = $2C^{12}H + 2NO^3 + NO^5 + 4HO$

Chryiodine, $C^{56}H^8N^3O^{28}$, or more probably a conjugate compound of $C^{28}H^4NO^{15}$ with $C^{28}H^4N^2O^{13}$, is formed from chrysammic acid by the action of the hydrate of sulphuric acid at a boiling temperature, with violent disengagement of hyponitric acid (nitric oxide gas). However, when the operation is conducted in a retort, sulphurous acid, carbonic acid and carbonic oxide can be detected among the products, while a portion of the acid is entirely destroyed. The chrysammic acid is converted into a violet substance, insoluble in water, which becomes gelatinous after washing and of a dark violet colour. Chryiodine of two different preparations gave—

Carbon	55·9	55·1	56 =	4206·72	55·1
Hydrogen	1·9	1·9	8	99·84	1·3
Nitrogen.....	6·5	6·2	3	525·00	6·9
Oxygen	35·7	36·8	28	2800·00	36·7

The formation of this substance from chrysammic acid results probably as follows:—

$$C^{56}H^8N^8O^{48} = C^{56}H^8N^3O^{28} + N^5 + O^{20}.$$

Chryiodine is converted by ammonia into two indigo-blue substances, one of which is a soluble amide, the other an insoluble ammonia compound.

On being heated with strong nitric acid, chryiodine disengages red vapours, and forms a red liquid, from which, on saturation with potash, no chrysammate of potash was obtained. In dilute potash it dissolves with difficulty, forming a violet liquid. Muriatic acid precipitates it from this solution as a violet gelatine.

Chryiodamide, $C^{28}H^8N^3O^{15}$, is the precipitate which falls, as above mentioned, when chryiodine is mixed with ammonia. It forms, after washing, an indigo-coloured substance, the composition of which, after drying at 248°, is, according to Van Tonningen—

Carbon.....	52·45	28	= 2103·36	52·4
Hydrogen	2·81	8	99·84	2·5
Nitrogen.....	14·03	3	525·00	13·0
Oxygen	30·72	13	1300·00	32·1

This substance is therefore an amide of one of the components of chryiodine, $C^{28}H^4NO^{15}$. When heated with a concentrated solution of potash, it does not lose its blue colour, and is not dissolved by it; but it parts with ammonia. The blue colour is likewise not altered by muriatic acid, in which it is equally insoluble.

Chryiodine with Oxide of Ammonium, $C^{28}H^{10}N^4O^{13}$, is left in the solution on treating chryiodine with ammonia. On evaporation it leaves a substance soluble in water. Dried at 248° it furnished—

Carbon	50·1	28	= 2103·36	49·8
Hydrogen.....	3·2	10	124·80	2·9
Nitrogen	16·4	4	700·00	16·5
Oxygen.....	30·3	13	1300·00	30·8

This substance is a combination of the second component of the chryiodine, $C^{28}H^4N^2O^{13}$, with 2 atoms of ammonia. The oxide of ammonium compound which originates from it is $C^{28}H^2O^{11}+2NH^4O$. It dissolves readily in potash, when ammonia is liberated, and the blue colour is converted into violet. On being heated with muriatic acid, it likewise exchanges the blue colour for a light violet one. After this loss of ammonia, it is nearly insoluble in cold water.

Chrysindine and Oxide of Ammonium, $C^{28}H^8N^5O^{13}$.—When chrysammic acid is heated with ammonia, and sulphuretted hydrogen passed through it, the liquid first becomes violet and then blue. A substance of the same colour is left undissolved. It is thrown upon a filter, and the liquid evaporated, when an indigo-blue residue is obtained. It is difficult to obtain the compound free from sulphur in this manner, which however is not essential to its constitution. Dried at 266°, analysis gave—

Carbon.....	45·4	47·5	28	48·0
Hydrogen	2·4	2·5	8	2·3
Nitrogen	19·2	20·1	5	20·0
Oxygen	28·6	29·9	13	29·7
Sulphur	4·4			

This substance appears to be produced by the sulphuretted hydrogen first forming aloetic acid, and from this and ammonia aloetinamide. 1 atom of nitric acid then separates from a double atom of the latter.

A substance, $C^{28}H^5N^4O^{13}$, is obtained when a solution of caustic potash is added to the solution of the preceding compound; it con-

tains NH^3 less, and is insoluble in potash. It is first washed with dilute solution of potash, and then with muriatic acid. This precipitate likewise contains some sulphur. Analysis gave—

Carbon	51·0	28	50·5
Hydrogen	2·1	5	1·5
Nitrogen.....	17·7	4	16·8
Oxygen	29·2	13	31·2

Schunck obtained a substance, on treating chrysammic acid with sulphuret of potassium, which he called hydrochrysammide, and the composition of which he calculated from his analyses to be represented by $C^{14}H^6N^2O^6$. But in this case the action is likewise more complicated, for the chrysammic acid is first converted by the sulphuret of potassium into aloetic acid, $C^{14}H^2N^2O^{10}$; and then this, by the exchange of O^4 for H^4, into $C^{14}H^6N^2O^6$. Schunck's name cannot be retained, because it gives a false idea of the nature of the substance. The separation of 4O is caused by the action of 4 atoms of sulphuretted hydrogen, which likewise produces the assimilation of H^4, 2 atoms of hyposulphurous acid being formed. There is, moreover, in this reaction, 1 equiv. nitric acid of the chrysammic acid, or, if it be preferred, of the aloetic acid, decomposed.

Chrysindamide, $C^{28}H^9N^5O^{18}$.—When chrysammic acid is dissolved in ammonia, sulphuretted hydrogen passed into it, and the whole boiled and filtered, the liquid furnishes on evaporation a blue sediment, which is the first product of the action of sulphuretted hydrogen upon chrysammide. It gives off ammonia when treated with potash. Rost van Tonningen obtained, on the analysis of this substance dried at 248°, and which was also not perfectly free from sulphur—

Carbon	42·83	34·4	28	43·0
Hydrogen	2·63	2·7	9	2·4
Nitrogen	17·30	17·5	5	17·9
Oxygen	35·84	36·4	18	36·8
Sulphur.....	1·40			

This substance is produced in the following manner :—

$$2(C^{14}H^4N^4O^{12}) - NO^5 + 2NH^3 - 2HO = C^{28}H^8N^5O^{17}.$$

When an excess of sulphurous acid is passed through the solution of chrysammic acid in ammonia, a brown liquid is obtained which is not precipitated by muriatic acid. When an excess of sulphurous acid is passed into chrysammic acid slightly heated in water, and ammonia is then added, the same brown colour is immediately produced. If an excess of sulphurous acid be avoided, a beautiful violet colour appears with perfect solution (as at the commencement on the passage of sulphuretted hydrogen). Muriatic acid disengages sulphurous acid from it, and precipitates a brown-violet gelatinous precipitate.—*Scheidk. Onderzoek.*, part v. p. 173.

PROCEEDINGS OF SOCIETIES.

British Association for the Advancement of Science.—Meeting held at Birmingham, September 12th, 1849.

The following are abstracts of the principal communications brought before the Chemical Section, as reported in the *Athenæum*:—

On the combined use of the Basic Acetates of Lead and Sulphurous Acid in the Colonial Manufacture and the Refining of Sugar. By Dr. Scoffern.

Dr. Scoffern stated the actual amount of pure white and crystallizable sugar existing in the sugar-cane juice to be from 17 to 23 per cent., and the amount of juice contained in the cane to be about 90 per cent. Of this amount only 60 per cent. on an average is extracted; and of this quantity only one-third part of its sugar is obtained, in a dark impure condition, instead of white and pure as it might be extracted. The operation at present generally followed in the colonial production of sugar involved the use of lime, an agent which, although beneficial in separating certain impurities and decomposing others, effects both these agencies at the expense of two-thirds of the original sugar. Various plans had been followed to avoid the use of lime. Alumina, in its hydrated condition, had been employed, but with inconsiderable success. As a purifying agent the basic acetate of lead was known to be most potent, but could not be generally employed, owing to the existence of no sufficient means of separating any excess of that agent which might remain. Dr. Scoffern effects this separation by means of sulphurous acid forced by mechanical means into the sugar solutions. The process had been used for more than twelve months in one of the large British refineries, and a lump of sugar prepared by means of the operation was exhibited. The advantages presented by this operation were thus summed up:—1. As applied to cane-juice, and other natural juices containing sugar, it enables the whole of the latter to be extracted instead of one-third, as is now the case; and in the condition of perfect whiteness, if desired, without the employment of animal charcoal. Owing to the complete separation of impurities, the juice throws up no scum when boiled, and therefore involves no labour of skimming. Finally, the process of curing is effected in less than one-third of the present time; and the quality of the sugar being in all cases so pure and dry, no loss in weight occurs during the voyage home. 2. As applied to the refinery operation, it enables the manufacturer to work upon staples of such impurity that he could not use them on the old process. It yields from these staples a produce equal in quality to the best refined sugars produced heretofore, in larger quantity and in less time. It banishes the operation of scum-pressing, the employment of blood and lime. Finally, its cost is even less than that of the present refinery process.

On the presence of Fluorine in the Waters of the Firth of Forth, the Firth of Clyde and the German Ocean. By G. Wilson, M.D.

In 1846 the author announced the discovery to the Royal Society of Edinburgh of fluorine as a new element of sea water. He was led to search for it, after observing that fluoride of calcium possesses a certain small but marked solubility in water, which explains its occurrence in springs and rivers, and necessitates its occasional, if not constant, presence in the sea. The only specimens of sea water he had examined before this summer were taken from the Firth of Forth at Joppa, about three miles from Edinburgh. He obtained the mother-liquor or bittern from the pans of a salt-work there, and precipitated it by nitrate of baryta. The precipitate, after being washed and dried, was warmed with oil of vitriol in a lead basin, covered with waxed glass having designs on it. The latter were etched in two hours, as deeply as they could have been by fluor-spar treated in the same way, the lines being filled up with the white silica separated from the glass. The author has recently examined in the same way bittern from the salt-works at Saltcoats, in the Firth of Clyde, but the indications of fluorine were much less distinct than in the waters on the east coast. On procuring, however, from the same place, the hard crust which collects at the bottom and sides of the boilers used in the evaporation of sea water, he found no difficulty in detecting fluorine in the deposit. This crust or deposit consists in greater part of sulphate of lime and of carbonate of lime and of magnesia; but it contains also much chloride of sodium, and the other soluble salts of sea water, entangled in its substance. When sulphuric acid, accordingly, is poured on it, it gives off much hydrochloric and carbonic, as well as some hydrofluoric acid; and the latter is thus swept away before it has time to corrode the glass deeply. The author preferred, nevertheless, to use the crust exactly as he got it, that the proof of the presence of fluorine might not be impaired in validity by the possibility of that substance being introduced by the water or reagents which must have been employed had the chlorides and carbonates been separated from the crust by a preliminary process. The crust, accordingly, after being dried and powdered, was placed along with oil of vitriol in a lead basin covered by a waxed square of plate glass, with letters traced through the wax. A single charge of the crust and acid corroded the glass very slightly; but by replenishing the basin with successive quantities of these materials, whilst the same plate of engraved glass was used as the cover, he found no difficulty in etching the glass deeply. Operating in this way, he has found fluorine readily in the boiler deposit from the waters of the Firths of Forth and Clyde. It is a less easy matter to subject the waters of the open sea to the requisite concentration before examination. It occurred to the author, however, that the incrustations which are periodically removed from the boilers of the ocean steamers would serve to determine the question whether fluorine is a general constituent of the sea. He made application, accordingly, at Glasgow and Leith, for the deposits in question. It appears, however, that the deep-sea steamers

which leave the former have their boilers cleaned out at other ports, so that he has as yet been unsuccessful in procuring crusts from the west coast of Scotland. He has obtained at Leith the crust from the boiler of a steamer called the Isabella Napier, which trades between that port and Wick; so that the greater part of the water consumed as steam by its engines is derived from the German Ocean, although a portion is necessarily obtained from the Firth of Forth. The crust from the boilers of this vessel was treated in the way described, and at once yielded hydrofluoric acid. A single charge indeed of the materials marked the glass distinctly, and four charges deeply. We may therefore infer that fluorine is present in the waters of the German Ocean, for different portions of the deposit yielded it readily, and marked glass as deeply as the deposit from the water of the Firth of Forth did, which could not have been the case if the whole crust had not contained fluorine pretty equally diffused through it.

From what is known of the comparative uniformity in composition of sea water, it may safely be inferred, that if fluorine be present in the waters of the Firths of Forth and Clyde, and in the German Ocean, it will be found universally present in the sea. Mr. Middleton, before 1846, came to the conclusion that fluorine must be present in sea water, since it occurred, as he had ascertained, in the shells of marine mollusca. Silliman, junior, without a knowledge of Middleton's views, drew the same inference from its invariable presence in the calcareous corals brought to America by the United States expedition from the Antarctic Seas. The author has found fluorine abundantly present in the teeth of the Walrus, which points to its existence in the Arctic Ocean; and it seems so invariably to associate itself with phosphate of lime, that it may be expected to occur in the bones of all animals marine and terrestrial. The author has found fluorine likewise in kelp from the Shetlands, but much less distinctly than he anticipated. Glass plates were only corroded so far as to show marks when breathed upon. Prof. Vœlker also was kind enough, at the author's request, to search for fluorine when analysing the ashes of specimens of the sea pink (*Statice Armeria*), which had grown close to the sea-shore, and contained iodine, and found fluorine in the plant. When all these facts are considered, it is not too much, the author thinks, to urge that fluorine should now take its place among the acknowledged constituents of sea water.

Prof. Forchhammer confirmed the results of Dr. Wilson. He had examined sea water from near Copenhagen, and found fluorine in every instance. He had also examined many shells and marine products from various localities, and they all gave the same body, the quantity of which was always greater in sea than in land animals.

On Phosphorus as producing cold short Iron. *By* Mr. Rinman.

This was a statement of the discovery in the Swedish iron of phosphorus whenever it presented the peculiarity of being cold short, as it is technically termed. The process adopted was the following :—The pig-iron, weighing about 3 grms. and reduced to small

pieces, was dissolved in diluted nitric acid, the solution evaporated to dryness, and the dry mass heated strongly with free access of air in order to destroy all carbon. After heating, the dry mass was triturated and mingled with 6 times its weight of soda, a little chlorate of potash and a little silica, and smelted as long as any gas was disengaged. The smelted mass was exhausted by boiling water, and digested for some hours. The solution was filtered, the undissolved residue washed with hot water containing a small quantity of chloride of ammonium. The solution was evaporated to dryness, and the dry mass treated with hydrochloric acid and dissolved in water. After filtration, the solution was neutralized, and the phosphate of lime was precipitated in a closed vessel by a solution of chloride of calcium with ammonia.

Inquiries on some Modifications in the colouring of Glass by metallic Oxides. *By* M. G. Bontemps.

In this communication some important practical points connected with the coloured ornamentation of glass and porcelain were brought forward. In the first place, it was shown that all the colours of the prismatic spectrum might be given to glass by the use of the oxide of iron in varying proportions and by the agency of different degrees of heat; the conclusion of the author being, that all the colours are produced in their natural disposition in proportion to the increase of temperature. Similar phænomena were observed with the oxide of manganese. Manganese is employed to give a pink or purple tint to glass, and also to neutralize the slight green given by iron and carbon to glass in its manufacture. If the glass coloured by manganese remains too long in the melting pot or the annealing kiln, the *purple* tint turns first to a light *brownish-red*, then to *yellow*, and afterwards to *green*. White glass in which a small proportion of manganese has been used is liable to become light yellow by exposure to light. This oxide is also in certain window glass disposed to turn pink or purple under the action of the sun's rays. M. Bontemps has found that similar changes take place in the annealing oven. He has determined, by experiments made by him on polyzonal lenses for M. Fresnel, that light is the agent producing the change mentioned; and the author expresses a doubt whether any change in the oxidation of the metal will explain the photogenic effect. A series of chromatic changes of a similar character were observed with the oxides of copper; the colours being in like manner regulated by the heat to which the glass was exposed. It was found that silver, although with less intensity, exhibited the same phænomena; and gold, although usually employed for the purpose of imparting varieties of red, was found, by varying degrees of heating at a high temperature and recasting several times, to give a great many tints, varying from blue to pink, red, opake yellow and green. Charcoal in excess in a mixture of silica-alkaline glass gives a yellow colour, which is not so bright as the yellow from silver; and this yellow colour may be turned to a dark red by a second fire. The author is disposed to refer these chromatic changes to

some modifications of the composing particles rather than to any chemical changes in the materials employed.

Report on the Heat of Combinations. By Dr. Andrews.

Every molecular change in the condition of matter is almost invariably connected with the evolution or the absorption of heat; and the quantity of heat thus set free or absorbed bears always a definite relation to the amount of the mechanical or chemical action. To ascertain this relation has been the object of Dr. Andrews in this investigation. The Report gives a general view of the actual state of our knowledge on the subject of thermo-chemistry. We cannot condense within the limits of our Journal the numerous points of interest involved in this Report. They are of the highest scientific interest, and will be published entire in the Journal of the Association. The following are a few of the principal points:— 1. The solution of a salt in water is always accompanied by an absorption of heat. 2. If equal weights of the same salt be dissolved in succession in the same liquid, the heat absorbed will be less on each new addition of salt. 3. The heat absorbed by the solution of a salt in water holding other salts dissolved is generally less than that absorbed by its solution in water. 4. The heat absorbed by the solution of a salt in the dilute mineral acids is generally greater than that absorbed by its solution in water. It was further shown by Dr. Andrews, that, in reference to the combination of acids and bases, the heat developed during the union is determined by the base, and not by the acid. An equivalent of the same base combined with different acids produces nearly the same quantity of heat. When a neutral salt is converted into an acid salt by combining with one or more equivalents of acid, no disengagement of heat occurs. When a double salt is formed by the union of two neutral salts, no disengagement of heat occurs. When a neutral salt is converted into a basic salt, the combination is accompanied by the disengagement of heat. When solutions of two neutral salts are mixed, and a precipitate formed from their mutual decomposition, there is always a disengagement of heat, which, although not considerable, is perfectly definite in amount. Numerous results illustrative of this point were given. The combinations of metals with acids, and their combustion in oxygen, were then examined. The actions of chlorine, iodine and bromine were also detailed, and the heat developed by the combination of these bodies with metals shown.

Prof. Magnus asked if Dr. Andrews had noticed any difference in the heat of combination of bodies in different allotropic states; as, for instance, the diamond, graphite and carbon.

Dr. Andrews stated that the diamond disengaged 7824 units of heat during its combustion in oxygen gas; in the form of graphite, 7778 units; and in that of wood charcoal, 8080.

On a new Method of determining the Organic Matter in Water. By Prof. Forchhammer.

The test which the author applies is hypermanganate of potash or soda, which he prepares by heating the hydrate of pot-

ash or soda with chlorate of potash and peroxide of manganese, according to the method of Wöhler. After heating, the salt is thrown into water, and so much diluted muriatic acid is added that it assumes a bluish-red colour; upon which carbonic acid gas is passed through until the colour has become bright red and the manganate of potash completely converted into hypermanganate. The liquid must be cleared, either by allowing it to deposit all the oxide of manganese, or by filtering it through asbestos. This liquid may be kept for a very long time unaltered in a glass vessel with a glass stopper. The next process is to ascertain the strength of the test, which is done by taking any determined measure of it, mixing it with water and a little alcohol, and then heating it. All the manganese is thrown down; and after being washed and exposed to a strong red heat, it is the manganoso-manganic oxide, $MnO + M^2nO^3$. This test is now applied in such a way that, for instance, one pound of the water which is to be tried is mixed with a small quantity of the test and boiled. If the colour has disappeared, another quantity is added, and the liquor again boiled, until, on going on in that way, the red colour of the liquid does not disappear any longer. After that, it is allowed to cool, and then the quantity of hypermanganate of potash, which has not been decomposed for want of organic matter in the water, is determined by comparing its colour with distilled water, to which have been added very small determined quantities of the test solution. If the quantity of the test which is thus added in excess is subtracted from the whole quantity which has been used, the real quantity of decomposed hypermanganic acid is determined, and thus also the quantity of organic matter itself. This method is liable to one fault, viz. that the nature of the organic matter may be different, and accordingly require different quantities of the test liquor to be decomposed. But the organic matter which generally occurs in water is nearly always identical with humic acid, and thus the determination of the organic matter allows it to be compared. As to that part of the organic matter in water which contains nitrogen, the author thinks that he has found out a method for determining it by itself; but not having yet finished his experiments on that point, he must leave it out of the question. Water taken from a greensand spring about twelve miles from Copenhagen contained so little organic matter that 1 lb. only required 6 measures of a test solution, of which 100 measures contained the manganese of 0·526 of the manganoso-manganic oxide; while 1 lb. of water taken from a lake which communicates with a peat moss required 74 measures of the same liquor. Prof. Forchhammer, continuing for a whole year every week the analysis of the water which is used for supplying Copenhagen, observed the following facts:—1st, the quantity of organic matter is greatest in summer; 2nd, it disappears for the most part as soon as the water freezes; 3rd, its quantity is diminished by rain; 4th, its quantity is diminished if the water has to run a long way in open channels.

On a continued spontaneous Evolution of Gas, at the Village of Charlemont, Staffordshire. By Mr. S. S. Howard.

In a field by the side of a lane near the village of Charlemont in Staffordshire, certain patches of ground had been noticed, which, without any apparent cause, were destitute of vegetation. They excited little attention, as they were supposed to be what are commonly called fairy rings; and it was not till the summer of 1846 that their true character was discovered. The person who first paid particular attention to the cause of these barren spots was the tenant of a neighbouring cottage (at which there is a cold bath noted in the vicinity for its sanative properties). From certain circumstances he was led to believe that something permeated the earth in those spots, and having dug a hole, he inserted a gas-pipe; and on applying a light to the mouth of the pipe, he found to his great surprise that a large flame issued from it. The escape of gas is larger in wet weather than in dry; but whether the gas is produced near the surface or otherwise has not yet been satisfactorily ascertained. The place where it issues from the earth is quite a mile from any coal-pit, and is outside the eastern edge of the Staffordshire coal basin. The gas, as analysed by myself from a portion of it (procured for me by Mr. S. Lloyd, Jun., of Wednesbury, about three miles from the place), was composed principally of light carburetted hydrogen. In 1000 vols. of the gas as it rises I procured 996 vols. of light carburetted hydrogen, 3 of carbonic acid, and 1 of aqueous vapour and nitrogen. Its specific gravity is 0·56126. Its composition is somewhat different from the gas known as marsh gas, and from that which collects in the old workings of mines, as it contains less carbonic acid and less nitrogen; the proportions in marsh gas of the former being $\frac{1}{20}$ and of the latter $\frac{1}{15}$ to $\frac{1}{20}$, whereas in this gas the proportions are only $\frac{3}{1000}$ and $\frac{1}{1000}$. It burns with a pale bluish-white flame, emitting considerable light and heat. Mixed with atmospheric air or oxygen, it explodes with considerable violence on contact with flame or with the electric spark. As it issues from the pipe it has a moist or slightly musty smell, as of sticks partially decomposed; but after keeping for some time in stopped glass jars, this is lost, and it becomes perfectly inodorous. When inhaled in large quantities, it produces the same effects as hydrogen gas; but it does not appear to exert any injurious influence on the health of the inhabitants of the cottage when diluted with a large portion of atmospheric air.

On the Composition of the Ash of Armeria maritima, *grown in different localities, and the Presence of Fluorine in Plants. By* Dr. A. Vœlcker.

The presence of iodine in plants growing near the sea, and the absence of that element in the same species of plants growing in inland situations, has been noticed some years ago by Dr. Dickie of Aberdeen, who likewise found that in the former, soda was more abundant, and potash prevailed in the latter. The author found Dr. Dickie's observations confirmed by his own, and no qualitative

analyses of the sea-pink (*Armeria maritima*) having been made, he analysed the ashes of specimens from three different localities, and submitted the results. Traces of fluorine, hitherto found only in few plants, were distinctly detected in all three ashes; iodine only in specimens grown near the sea shore.

Analytical Investigations of Cast Iron. By Mr. F. C. Wrightson.

This series of analyses showed the influence of the hot blast in producing the so-called "cold short iron," by occasioning an increased reduction of phosphoric acid, and the consequent increase of phosphorus in the "hot-blast" iron. The respective per-centages were—

	I.	II.	III.	IV.	V.	VI.	VII.
Cold blast.....	0·47	0·41	0·31	0·20	0·21	0·03	0·36
Hot blast.....	0·51	0·55	0·50	0·71	0·54	0·07	0·40

The irons differed also considerably as to the state in which the carbon was contained in the hard white iron, resembling impure steel, containing nearly all its carbon in a state of chemical combination, whilst the carbon in the gray and mottled varieties of iron was principally contained only as a mechanical mixture. The presence of sodium and potassium in all the specimens examined was also noticed for the first time, and it was thought probable that these might materially affect the qualities of the metal.

On Copper containing Phosphorus, with details of Experiments on the corrosive Action of Sea-Water on some varieties of Copper. By Dr. Percy.

Upon analysing a specimen of copper, to which when in a state of fusion some phosphorus had been added, it was found that it contained a considerable quantity of phosphorus, and also a large portion of iron derived from an iron rod employed in stirring the mixture at each addition of the phosphorus. The copper employed was of the "best selected;" it appeared to be harder than copper treated with arsenic. The details of the analysis of 116·76 grains were given, the result of which was—

Phosphorus	0·93
Iron	1·99

A second analysis gave—

Copper.....	95·72
Iron.....	2·41
Phosphorus.....	2·41
	100·54

It has long been stated that a very small quantity of phosphorus renders copper extremely hard, and adapts it for cutting instruments; but such an alloy as that formed by Dr. Percy had not previously been formed. It is a remarkable fact that the presence of so large a quantity of phosphorus and iron should so little affect the tenacity and malleability of the copper. The effect also of phosphorus in causing soundness in the casting of copper is interesting,

and may be of practical importance. Some experiments were next described, made by Captain James of Portsmouth, bearing on the œconomic value of the alloy of phosphorus and copper. By the experiments made by Captain James on the corrosive action of sea-water, it would appear that this compound was much less affected than most other specimens of copper tried. The results derived from exposing measured pieces of copper to the action of sea-water for nine months were as follows:—

Electrotype copper, loss per square inch	1·4	grains.
Selected copper	1·1	...
Copper containing phosphorus	0·0	...
Copper from the "Frolic"	1·12	...
Dockyard copper, No. 1.....	1·66	...
„ „ No. 2.....	3·00	...
„ „ No. 3.....	2·48	...
„ „ No. 4.....	2·33	...
Muntz's metal.....	0·95	...

The results appear to be of sufficient importance to excite attention to the fact, and to elicit further inquiry, especially when it is remembered how important and œconomic a desideratum it is to the Admiralty to diminish or prevent the corrosive effect of sea-water upon copper.

On the Formation of Dolomite. By Prof. Forchhammer.

Prof. Forchhammer stated that the white chalk of Denmark is covered by a bed only a few feet thick, containing corals of the genera Caryophyllia and Oculina, and a number of fossils different from those of the white chalk; that this bed, which may be seen over a great part of Denmark always in the same position, the same fossiliferous character, and the same thickness, in the hill of Faxöe is enlarged to a thickness which cannot be much less than 150 feet. Here the Faxöe limestone is covered by a bed of dolomite, which again is covered by a bed of limestone, consisting almost entirely of fragments of Bryozoa, and belonging likewise to the chalk formation. The limestone of Faxöe contains about 1 per cent. of carbonate of magnesia, arising from the shells and corals which always contain it in small quantity, but which in some instances, as in the Isis and some Serpulæ, amounts to 6 or 7 per cent. The bryozoan limestone which covers the dolomite does not contain more than 1 per cent. of carbonate of magnesia, while the dolomite contains 16 or 17 per cent. of carbonate of magnesia. The dolomite occurs generally in round globular masses, very similar to those of Humbledon Hill, and are evidently like most of the globular masses of limestone, such as confetti di Tivoli and the peastone from Carlsbad, the produce of springs; an opinion which is still more confirmed by a number of large vertical tube-like cavities, which pass through the compact limestone, and are completely similar to those described by several English geologists as passing through the chalk, which have been recognized as the natural pipes of springs. Thus the Faxöe dolomite is the produce of springs; but then these springs

have deposited stalagmitic limestone wherever they have passed through the crevices of the limestone rock, which, as a more or less thick coating, covers all the fossils. Now this produce of the springs contains only a very small quantity of magnesia, but, besides lime, a great quantity of oxide of iron. It appears therefore that the springs do not deposit carbonate of magnesia if no other reaction takes place than the escape of carbonic acid; but that the dolomite is formed where the carbonic acid springs come in contact with sea water. The author has made a great number of experiments on the decomposition which takes place when water containing carbonates dissolved by carbonic acid acts upon sea water, and found that always a more or less great quantity of carbonate of magnesia was precipitated with the carbonate of lime. When using water containing only carbonate of lime, the quantity of carbonate of magnesia thrown down at a boiling heat amounted to 12½ per cent., the rest being carbonate of lime. The results of this decomposition vary however very much, and according to conditions not yet well known. So much however may be stated, that the quantity of carbonate of magnesia precipitated increases with the increasing temperature. Water which, besides carbonate of lime, contains carbonate of soda, throws down a much larger quantity of carbonate of magnesia, amounting in one experiment to 27·93 per cent. of the precipitate. At last the author tried what kind of precipitate some of the most famous mineral springs of Germany would form if they at the boiling-point acted upon sea water. Thus he obtained—

From the water of Selters.

Carbonate of lime	86·55
Carbonate of magnesia	13·45
	100·00

From the water of Pyrmont.

Carbonate of lime	84·30
Carbonate of magnesia	5·12
Protoxide of iron	10·50
	100·00

The oxide of iron in the experiment was of course precipitated as peroxide of iron, and from that the carbonate was calculated.

From the water of Wildengen.

Carbonate of lime	92·12
Carbonate of magnesia	7·88
	100·00

On an Improvement in the Preparation of Photographic Paper, for the purpose of automatic Registration, in which a long-continued action is necessary. *By* C. Brooke.

The preparation of the paper described may be thus briefly stated:—The paper is washed over by a brush with a solution of 12 grs. of bromide of potassium, 8 grs of iodide of potassium and

4 grs. of isinglass in 1 fluid ounce of distilled water, and dried quickly. When about to be used, it is washed over by a brush with a solution of 50 grs. of nitrate of silver to 1 fluid ounce of water, and placed on the cylinder of the registering apparatus, on which it remains in action for twenty-four hours. When removed, the impression is developed by brushing over a warm solution of gallic acid, containing 20 grs. in the fluid ounce, to which a little strong acetic acid is added, and is then fixed with a solution of hyposulphite of soda in the usual manner. The present improvement consists in rinsing the paper in water after the application of the solution of nitrate of silver, pressing out the superfluous moisture in folds of blotting-paper, and then adding a little more of the solution of nitrate of silver to the surface of the paper. This is most conveniently effected by pouring a small quantity on the paper, and then pressing a glass rod or tube lightly over the paper, by which the solution is evenly distributed over the surface, and the contact of organic matter avoided. The increased sensibility and improved cleanliness of the paper consequent on this addition to the process are presumed to depend on the removal by washing of the nitrate of potash formed by the mutual decomposition of the salts on the surface of the paper.

PATENT.

Patent granted to John Mitchell, Henry Alderson, *and* Thomas Warriner, *for improvements in smelting copper.*

This invention consists of improvements in obtaining metallic copper from certain copper ores and other substances containing copper. The substances which are intended to be treated by the methods to be described are,—1st, the sulphurets of copper; 2nd, the sulphurets of copper mixed with any other metallic sulphuret or sulphurets; 3rd, a sulphuret of copper containing a sulphate or other salt of copper; 4th, sulphuret of copper mixed with any other metallic sulphuret or sulphurets containing a sulphate or other salt of copper; 5th, carbonates or oxides of copper; 6th, a mixture of carbonate and oxide of copper containing a sulphuret of copper or a sulphuret of other metal; 7th, a carbonate or oxide of copper, or a mixture of a carbonate and oxide of copper with a sulphuret of copper mixed with other metallic sulphurets; 8th, a mixture of any of the above carbonates or oxides or carbonates and oxides with a metallic sulphuret or sulphurets and a sulphate or other salt of copper; 9th, carbonate or oxide of copper, or a carbonate and oxide of copper mixed with a sulphate or other salt of copper.

In the ordinary method of copper smelting, the sulphuret ores are subjected to a numerous series of alternate roastings and fusions, the ultimate object of which is to convert all the sulphur they may contain into sulphurous acid, and the iron and the copper into oxides; the oxide of iron passes off in the siliceous slag, whilst the

copper is concentrated in the regulus, which at last is brought into such a state, by the above operations, that it contains but little sulphur and iron; both of which substances are removed by the refining process, which in this stage it has to undergo; and the copper thus produced is either cast into ingots, or is submitted to another operation, by which it acquires the desired degree of malleability.

It is therefore evident that the object of all the above operations is to remove the sulphur and iron: this is done progressively and at the same time in the process just described. This object the patentees propose to effect by two distinct operations. By the first the sulphur will be entirely removed by treating a rich ore, or a regulus (obtained without the addition of iron or alkali), in a finely divided state, in the manner to be hereafter described; and by the second the iron will be separated, and the copper obtained in a comparatively pure state, by treating the mixed oxides, resulting from the first operation, with siliceous and carbonaceous matters, without the use of iron, or the application of electric currents.

Thus, by the new process, the smelting or production of copper from copper ores is effected by fewer operations, and in a much shorter time, than in the ordinary process. In many cases but one roasting and one fusion will be necessary, and in others, at most, two roastings and two fusions.

The chief difficulty in getting rid of the last traces of sulphur depends upon the circumstance that, during the ordinary roasting of sulphur ores of copper, the whole of the sulphur is not expelled in the gaseous state as sulphurous acid, but a portion is converted into sulphuric acid, which unites with a corresponding equivalent proportion of oxides of copper and iron to form sulphates of copper and iron. This however is not all, for if lime, baryta, strontia, or magnesia be present, either in the caustic or carbonated state, then a still greater quantity of sulphuric acid is retained by those bases to form sulphate of lime, baryta, strontia, or magnesia. Now, the patentees have found that whilst sulphates, either of copper, iron, lime, baryta, strontia (these three latter sulphates may be disregarded in practice, as the results they produce are not sufficiently marked to be injurious), and magnesia are present, on reducing the mixture of oxides of copper and iron, and the sulphates of iron, copper, &c., the latter are decomposed, giving rise to the production of sulphurets of iron and copper in addition to the metallic copper and iron produced, so that a very considerable portion has to undergo a further roasting. In the new process about to be described, this difficulty is overcome. Again, when a mixture of oxides of copper and iron, free from sulphur, is to be reduced, it will be found that copper is indeed separated, but containing a very large quantity of iron; the copper so produced would therefore have to be refined, in order to fit it for the market. This is avoided by forming silicates of copper and iron, and then reducing by carbonaceous matter: the silicate of copper is completely reduced and separated, whilst the silicate of iron is left intact.

Owing to the influence of the presence of lime, baryta, strontia, and magnesia (more especially the latter earth) on the roasting process, it is found desirable to divide all copper ores, and other substances enumerated as susceptible of treatment by the present process, into two grand classes, thus:—

1st Class. Those ores or substances containing neither lime, baryta, strontia, nor magnesia, in the caustic or carbonated state, or in the state of sulphate.

2nd Class. Those ores or substances which contain lime, baryta, strontia, or magnesia (more especially the latter), in the caustic or carbonated state, or in the state of sulphate.

These classes are each subdivided into two orders, viz.—

Order 1. Those ores or substances which contain more than 25 per cent. of copper.

Order 2. Those ores or substances which contain less than 25 per cent. of copper.

All ores and other substances enumerated as susceptible of treatment by the present process, and which belong to Class 1, may be treated according to Process No. 1, whether they belong either to Order 1, or 2.

Process No. 1. *Treatment of copper ores of the* 1*st Class.*—The finely-pulverized (fine dressed) ore is placed in a reverberatory furnace, known as a "calciner" (a furnace constructed according to Sheffield's patent, having air passing through openings in the bridge over the roasting ore in the furnace, is preferred), and exposed to a gradually increasing temperature, until it arrives at a full red heat. During the whole of the time it is in the furnace it is stirred from side to side, and from end to end, in order to expose the greatest possible surface to the oxidating action of the heated atmospheric air passing over the roasting matter. This is to be continued until the ore ceases to smell of sulphurous acid. The heat is now to be increased as much as possible, taking care, however, that the heated ore does not, in the slightest degree, agglutinate (this point must be particularly attended to),—the stirring all this time being constant. The object of the increased heat is the decomposition of the sulphate of copper, formed during the earlier stage of the roasting. At the higher temperature this salt is decomposed and its acid expelled. This may be facilitated by the addition of small quantities of any carbonaceous matter, as is already known. After it has been in this state about half an hour, a sample is to be taken out, mixed with a small quantity of water, and well stirred, allowed to settle, and the clear supernatant liquid poured off. If, on the addition of solution of ammonia, the liquid assumes a blue tint, or on the addition of ferrocyanide of potassium, a reddish tint, the heat is to be continued for another half-hour; after which time it is again to be tested in the same manner, and so on, until no copper can be detected in the aqueous solution. The ore may now be drawn from the furnace, and is ready for the reducing operation to be hereafter described.

Process No. 2. *For ores and substances of the* 2*nd Class, enumerated as susceptible of treatment by this process.*—The finely-pul-

verized ore is to be roasted precisely as described for ores of Class No. 1; but, before being ready for the reducing process, it has to undergo the following operation, which has for its end the separation of the sulphate of magnesia which has withstood decomposition (as before stated, the danger attached to the presence of the sulphate of lime, baryta, and strontia, is so small, that in practice it may safely be disregarded):—The roasted ore, while still hot, is conveyed into a tank (provided with a false bottom) containing a considerable quantity of water, and well agitated; after having remained in the water about three or four hours, with occasional agitation, the water, containing sulphate of magnesia in solution, is run off from the bottom of the tank; and the ore, thus washed, is allowed to drain as much as possible. It is then removed and dried, and is fit for the reducing process.

When the ore contains less than 25 per cent. of copper (Order 2nd) it is thrown into a "fusion" or "metal" furnace, with a certain quantity of lime or old slag, as is usual in such operations; and the regulus so produced is run into sand moulds or into water. It is preferred to give the ore a partial roasting before forming a regulus, as in the following process:—The finely-pulverized ore is placed in the furnace already described, and exposed to a dull red heat until very little or no more sulphurous acid can be smelt. The ore is then removed to another reverberatory furnace, known as a fusion or metal furnace, and mixed with an appropriate quantity of lime or lime and old slag, to form a fluid mixture when exposed to a sufficient temperature. When the whole is well fused, the furnace is tapped, and the regulus run into either sand moulds or water. The regulus produced by either of the preceding methods is reduced to a state of fine division, and in that state it is roasted, exactly as described for ores and substances under Process 1, Class 1; after which it is ready for reducing.

Reducing Process.—The roasted ore or regulus is mixed with such a proportion of sand as will correspond to the amount of oxide of copper and oxide of iron in the substance. Thus, if the mixed oxides consist of about 88 per cent. of oxide of copper, and the remainder be oxide of iron, from 35 to 40 per cent. of sand is required, with such a quantity of lime or old slag as will cause the whole to flow freely. On adding the sand and lime, or the sand and slag, coal or other carbonaceous matter is to be added, in the proportion of about one-tenth of the weight of the sand and lime, or sand and slag. When the whole is well fused, a further portion of coal or other carbonaceous matter is to be added to the fused mass and well stirred together; the heat is then to be increased for a short time, and the whole well stirred again. A portion of the slag is now to be taken out, and tested for copper by any ordinary method; if but traces be present, the operation is finished, and the furnace may be tapped; but if copper be present in quantity, more coal or carbonaceous matter must be added, and the mass must be again stirred, and so on until the slag is nearly free from copper, as above.—Sealed, December 28, 1848.

THE CHEMICAL GAZETTE.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Production of Æthers by the Action of Potash upon the Balsams. By Prof. E. A. Scharling *of Copenhagen**.

On the 19th of January 1849, the author communicated to the Royal Danish Academy of Sciences a preliminary statement of some experiments made in order to produce æthers by acting with potash on various natural balsams. After having noticed the earlier investigations on Peruvian balsam, he observes that the formula given by Fremy for the composition of cinnameine, $C^{54} H^{26} O^{3}$, may be looked upon as $2(C^{16} H^{7} O^{2}) + C^{22} H^{12} O^{4}$, of which the first member represents the formula for cinnameine given by Plantamour, and the second member that for cinnamic æther, which the latter chemist produced from Peruvian balsam. Plantamour, however, having used alcohol in his investigations, doubts might arise whether this had not occasioned the formation of the cinnamic æther. The author submitted 1 part of Peruvian balsam and 2 or 3 parts of solution of potash, of the specific gravity 1·3, to distillation, after the mixture had been left for twenty-four hours. The product consisted of water and two oily bodies, the one lighter, the other heavier than water. By drying and redistillation, the heavier liquid was obtained perfectly transparent, of high refractive power, of specific gravity 1·03, and with a boiling-point of 401° F. Immediately after the distillation the smell was faint; but after having stood for a while it became aromatic, like that of cinnamic æther.

Immersed in a refrigerating mixture of snow and rock-salt, the whole remained liquid at 5° F. The oily liquid, of less specific gravity, boiled at about 356°; its specific gravity was less than that of water; the smell not unlike aniseed; the taste sweetish, aromatic. Cooled to 5° F., the greatest part congealed. Both these liquids are altered by distillation; for even when heated in an oil-bath, they assume a light wax-yellow colour before they begin to boil. As both these liquids thus offered great resemblance to cinnamic æther and peruvine, the author tried to ascertain their identity with these substances by treating them with hydrate of potash and sulphuret of carbon. Although the discoverer of xanthogenic acid, the late Prof. Zeise, remarks that æther and sulphuret of carbon with hydrate of

* Communicated by the Author.

potash do not give xanthogenate of potash, yet it was presumed that this salt might be produced by treating compound species of æther with hydrate of potash and sulphuret of carbon. As this supposition has been fully confirmed with different kinds of æther, for instance with acetic æther, the author mixed separately both the liquids produced by Peruvian balsam with powdered hydrate of potash and sulphuret of carbon. In both these experiments the mixtures congealed; and when samples of the saline mass were dried between paper, and then dissolved in water and tested with salts of copper and lead, they furnished yellow xanthogenate of copper and white xanthogenate of lead. Hence there can be no doubt that the liquid of higher specific gravity contains cinnamic æther, obtained for the first time without any addition of alcohol. How far the liquid of less specific gravity is peruvine or a mixture of peruvine and cinnamic æther, the author hopes to be enabled to state more fully in a subsequent communication. By distilling the solution of potash, which had been separated from the cinnameine, only traces of an oily liquid were obtained; the rest of the distillate appeared to be water. Hence it is evident that even at the ordinary temperature, and by the influence of a solution of potash, the combination, which at a suitable temperature is converted into a species of æther, is decomposed. By distilling Peruvian balsam with water, no oil or æther, as is known, is produced. Since this possibly might arise from the boiling-point of cinnamic æther lying too high, the author distilled a portion of Peruvian balsam with a solution of mineral salt and a smaller portion of balsam with a concentrated solution of chloride of zinc. The last distillation was performed by dropping the balsam gradually into the boiling saline solution. By this process, besides water, some cinnamic acid, and a very little quantity of two liquid oily brownish bodies, the one of greater and the other of less specific gravity than water, were obtained. Both had an empyreumatic odour; and when boiled with water, a quantity of crystals of cinnamic acid were obtained by cooling. The author could discover no trace of cinnamic æther in this distillate. By subjecting Peruvian balsam to dry distillation, several oily liquids were obtained, containing a great quantity of cinnamic acid, as also water. The cinnamic acid crystallized on cooling, and was collected on a filter; the liquid that had passed through, after it had been dried over chloride of calcium and redistilled, was treated with powdered hydrate of potash and sulphuret of carbon. No traces of xanthogenic acid could be detected in this mixture.

A portion of Peruvian balsam was next operated upon with a solution of carbonate of soda. The watery solution obtained behaved like a solution of cinnamate of soda. The remaining substance was dried, dry carbonate of soda added to it, and the mixture subjected to destructive distillation. The product resembled in appearance the products from the dry distillation of the Peruvian balsam; but in this traces of xanthogenic acid were found by suitable treatment. From these experiments, therefore, it is not to be

concluded *that cinnamic æther pre-exists in the balsam, but that it is most likely formed by the action of strong bases.*

E. Simon's investigation on liquid storax has made us acquainted with a body which he calls styracone. The author found that on treating liquid storax in the same manner as he had treated Peruvian balsam, he immediately obtained a distillate, from which, after standing for a while, a body separated, which possessed all the properties assigned by Simon to styracone. Moreover, it easily dissolved in alcohol of 0·851 spec. grav. By treating the styracone with powdered hydrate of potash and sulphuret of carbon, xanthogenate of potash was formed amongst other products. Hence it is supposed that the styracone constitutes a compound æther, and the author intends investigating it more minutely. From want of styrole, he examined how benzole would act with hydrate of potash and sulphuret of carbon. No xanthogenate of potash was produced. Balsam of copaiva was next treated with hydrate of potash, and then distilled. A considerable quantity of oil, which floated on the distilled water, was immediately obtained. When the water had been poured back and distilled a second time, the quantity of oil collected constituted about 5 oz., and the distilled water about four times as much. A pound of balsam and a pound and a half of solution of potash (spec. grav. 1·25) had been used. The oil did not appear to differ from that of balsam of copaiva, which occurs in trade; but on treating these oils with hydrate of potash and sulphuret of carbon, no formation of xanthogenate of potash could be perceived. Copaivic acid, however, not being of a volatile nature, the author has not given up the hope of producing an æther by the action of a solution of potash from this balsam by a somewhat altered process. By treating Venetian turpentine in a similar manner, an oily liquid was obtained, which, when dried over chloride of calcium or lime, did not appear to be acted upon by powdered hydrate of potash. For several hours after the addition of the potash, the colour of the liquid remained unaltered, and exhibited no change of temperature. On adding sulphuret of carbon, a white saline mass was formed after some time, which gradually caused the whole mixture to congeal into a jelly. After twenty-four hours this jelly was thrown upon a filter; and when the greater part of the liquid which the mass contained had run off, the residue was most carefully pressed between paper. A part of the saline mass thus obtained was dissolved after being dried; another portion was shaken with æther, in order to remove all adherent oil and resin. The æther was separated by filtration, and the saline mass, after being dried, was likewise dissolved in water. Both these solutions immediately produced brown precipitates with dichloride of copper, but which after some time became yellow.

With nitrate of lead, whitish-yellow precipitates were produced; and with several other solutions of salts, similar reactions to those produced by xanthogenic acid, except that all the precipitates had in general a somewhat darker colour. This circumstance led to the supposition that an æther had been formed by the action of the potash on the Venetian turpentine. The boiling-point of the distillate

was about 307° F.; its specific gravity 0·87; the solubility in alcohol of 0·823 spec. grav. was identical with that of common oil of turpentine.

These properties agree so nearly with those of common turpentine oil, that the supposition of the liquid being a species of æther was abandoned; whereas it was presumed that if Venetian turpentine was distilled with water, the oil obtained would exhibit the same relations to hydrate of potash and sulphuret of carbon as the above-mentioned liquid. Experiment gave an affirmative answer. Common oil of turpentine, recently distilled and well freed from water, was treated as above. The results, upon the whole, were the same; consequently it is possible to produce, by the action of hydrate of potash and sulphuret of carbon, from pure turpentine oil, a combination possessing great resemblance to xanthogenic acid. But in order to form this substance, it is absolutely necessary to have well-fused hydrate of potash; because in the state in which it is often met with in commerce it contains too much water. The whole of the turpentine oil cannot be decomposed by the sulphuret of carbon and hydrate of potash. The same appears to occur in this decomposition as in the production of terpine; a part only of the turpentine oil enters into the new combination.

The author observed, that though it is asserted that all pure turpentine oil consists only of $C^{10} H^8$, and that the boiling-point and the specific gravity are alike, yet the oil from Venetian turpentine appears in several respects to differ from the oil of common turpentine. Thus the last-mentioned oil is speedily coloured by the hydrate of potash, which is not the case with the oil of Venetian turpentine. The latter oil polarizes the light to the left; but only a rotation of 25° is required to produce the violet colour. The same is the case with a saturated solution of muriate of dadyle in alcohol when the dadyle has been prepared from Venetian turpentine.

Common turpentine oil also polarizes the light to the left; but to produce the violet light a rotation of 70° is required. This also happens both with a saturated alcoholic solution of muriate of dadyle prepared from common turpentine oil, and the liquid part of that turpentine oil from which the compound resembling xanthogenate of potash had been produced. The longer the turpentine oil has been kept, the stronger is it acted upon by the hydrate of potash. It is owing to this circumstance that at times it produces an increase of temperature of more than 108° F.; then forms a clear brown gelatinous mass, which appears in a great measure to prevent the production of the compound resembling xanthogenate of potash. Even when common turpentine, recently rectified and dried over lime, is employed for the preparation of this salt, a much darker product is generally obtained than with oil from Venetian turpentine. By allowing the saline mass, which in general contains potash and sulphuret of potassium, to remain exposed to the air, the substance becomes clearer, and the precipitate produced by sulphate of copper becomes yellow much sooner.

The author has not yet succeeded in obtaining the compound

resembling xanthogenate of potash from *terpine*; whether it can be procured from *terpinole* he has hitherto had no opportunity of ascertaining. The author intends making similar experiments with several other essential oils, the results of which will be communicated hereafter.

Observations on Cardamine amara, *Horseradish and Myronic Acid. By* F. L. Winckler.

The author has examined the dried herb of *Cardamine amara*, which had been collected just before flowering. Its taste was more bitter than acrid. According to his experiments, it contains a sulphuretted and nitrogenous acid, most probably identical or very closely allied to the myronic acid of mustard seed, combined in the plant with an organic substance, and which, both alone as well as in combination with bases, forms with myrosine of yellow mustard seed, but not with emulsine of almonds, an acrid volatile oil resembling the oil of horseradish. Considering the intense bitterness and the slight acridity of the herb, it is not probable that a substance acting the part of the myrosine is present in the herb.

Fresh roots of horseradish, which even on grating disengaged a volatile oil, lost their acridity on being heated for some time in the water-bath under alcohol. The alcohol which distilled over was not acrid, and contained no volatile oil, for it was not rendered turbid by water. The spirituous extract deposited, on distilling off the alcohol, a dirty green fatty mass, which was removed. The remaining filtered aqueous liquid left on evaporation an amorphous brownish-yellow residue. Alcohol of 0·863 spec. grav. dissolved a portion, leaving an insoluble residue of sugar; the solution, on being again evaporated with myrosine from mustard seed, disengaged oil of horseradish, and still contained sugar, for on oxidation there was formed along with sulphuric acid some oxalic acid.

Absolute alcohol removed a substance from this mass without acquiring any perceptible colour, and which collected in the form of a powder over the smeary sediment, and was separated by decantation. This latter substance will undoubtedly prove to be highly interesting, and the author promises to furnish a more accurate examination of it. From the experiments he has hitherto made, it appears to be a combination of a sugar with potash, which seems to be combined with myronic acid in the horseradish. In the treatment above described this acid could be detected, by means of myrosine, in the smeary sediment beneath the absolute alcohol after it had been dissolved in water, whilst the alcohol contained no compound of myronic acid, but first took up the compound of sugar and potash and then deposited it, and on the addition of an alcoholic solution of potash deposited still more of the compound in the form of a snowy-white powder; there was still more sugar and potash contained in the smeary sediment. This sugar could not be obtained crystallized after separation from potash by means of sulphuric acid and removing the excess of acid by baryta. The com-

pound of sugar and potash dissolves in hot alcohol when no excess of potash is present, which renders it brown, without decomposition, and again separates from it as a fine white powder. The isolated sugar dissolves in cold alcohol. To obtain more of this sugar, the author agitated syrup with eight times its quantity of absolute alcohol, decolorized the clear decanted liquid with animal charcoal, and mixed it with a solution of potash in alcohol. In this manner he procured a large amount of this compound of sugar and potash, which possessed all the properties of the substance obtained from the horseradish.

According to the above experiments, myronic acid is most easily prepared by fermenting the residue from the alcoholic extract of the horseradish after distilling off the alcohol in order to destroy the sugar. On evaporating the fermented liquid, a bitter syrup is obtained, which contains acid myronate of potash. No volatile oil is formed in this fermentation.—*Journ. für Prakt. Pharm.*, vol. xviii. p. 89.

On the Production of Organic Bases from Nitrogenous Vegetable and Animal Substances. By Dr. J. Stenhouse.

[Concluded from page 395.]

By boiling with Alkaline Solutions.—Starting from the facts hitherto stated, I think we have every reason to assume, that when in the dry distillation of vegetable or animal substances ammonia is produced in considerable quantity, it is always accompanied by simultaneously-formed organic bases. Now since ammonia may be obtained, as is well known, from these substances by several other methods, it appeared by no means improbable that in these cases organic bases would likewise be formed. It has long been known that ammonia is given off in abundance when the nitrogenous constituents of plants or animals are boiled with strong alkaline leys. A certain quantity of beans was therefore boiled in a large still with caustic soda. They were soon converted into a dark-coloured mucilage, a consistence which proved a great hindrance to the progress of the distillation from the frothing and boiling over; it was therefore only possible to distil small quantities at a time and with a moderate fire. On carefully rectifying the distillate, a clear strongly-alkaline liquid was obtained; it contained a large amount of ammonia, a small quantity of an agreeably-smelling aromatic oil, and a tolerable amount of organic bases. The liquid was neutralized with muriatic acid, and the oil separated by means of a moistened filter. On supersaturating with caustic potash, there was obtained with the ammonia the organic bases partly floating on the liquid and partly dissolved in it. They had every resemblance to those obtained by dry distillation, but at present I am not able to say whether they are identical or not. Oil-cake was distilled in the same manner, and similar results were obtained; the same may therefore be expected from the corresponding nitrogenous parts of other plants.

Organic Bases from Flesh by boiling with Caustic Alkalies.—A bullock's liver, cut into small pieces, was submitted to distillation with caustic soda. It dissolved quickly into a brown strongly-frothing gelatine, and a very alkaline liquid passed over, accompanied by an agreeably-smelling aromatic oil. On saturating the liquid with muriatic acid and evaporation, this oil is converted into a brown resin. The concentrated liquid furnished, on supersaturation with soda and distillation, an ammoniacal solution of oily bases, of which a quantity separated on the surface. At the present moment I am unable to state anything respecting their nature. The employment of caustic leys instead of dry distillation has at least the advantage that the bases are obtained at once free from empyreumatic oils and resins.

Production of Organic Bases with the aid of Sulphuric Acid.—A small quantity of beans were digested with sulphuric acid, which had been previously diluted with 3 or 4 parts water; they were soon reduced into a pasty mass. Care was taken not to allow the action of the sulphuric acid to proceed to the production of sulphurous acid. The acid liquid was supersaturated with carbonate of soda and distilled. The ammoniacal liquid which passed over likewise contained organic bases similar to those previously described.

Organic Bases by Putrefaction.—The author, who states that he has not yet had any opportunity to ascertain whether the production of ammonia in this case is accompanied by that of organic bases, observes that he should not be at all surprised if putrefaction were, from the less energetic kind of action, to prove the most advantageous method for the preparation of organic alkaloids on a large scale.

Guano.—An aqueous solution of Peruvian guano was submitted to distillation with an excess of caustic lime. The strongly-ammoniacal distillate was neutralized with muriatic acid, and evaporated to about one-third. After supersaturating with soda, it was again submitted to distillation. The product contained a small, but still distinct trace of basic oil, resembling that obtained from other substances. It dissolved readily in muriatic acid to a perfectly clear liquid, and was again separated by alkalies. It appeared to be far more soluble in water than the previously-mentioned basic oils. The amount however was much smaller than I had expected, although guano must not be selected as a fair example of the effect of putrefaction on complex nitrogenous substances, as the greater portion of the nitrogen contained in it exists originally in the form of ammoniacal salts. The above experiment nevertheless shows that guano likewise contains volatile organic bases besides ammonia.

Starting from the above data, I think we may state with tolerable certainty, that "in all cases where ammonia is produced in large quantity, either from complex animal or vegetable substances, it is constantly accompanied by the production of a larger or smaller quantity of volatile organic bases." When therefore seeds and leaves of different genera of plants are subjected to these or analo-

gous processes, we have every reason to expect that the number of organic alkaloids will soon be considerably increased.

Another conclusion which I think may be drawn with equal justice from these experiments is, that the nitrogenous principles of plants, as vegetable fibrine, albumen, caseine, &c., although very analogous, are nevertheless not identical with the corresponding principles of the animal kingdom, as otherwise their products of decomposition should likewise be identical. The same series of bases would have been obtained from beans and bones, as well as from other vegetable and animal substances, on submitting them to the same processes of decomposition. Since this, as we have seen, is not the case, I think I am justified in assuming that animal and vegetable fibrine, caseine, &c., although very analogous, are not identical substances, which has hitherto been the view entertained by some of the most celebrated chemists.

In carrying out the dry distillation both of animal and vegetable substances, great care should be taken to keep the temperature as low as possible; for I have frequently observed that when accidentally the heat was raised too high, the organic bases were nearly entirely destroyed, so that in this case ammonia was almost the only alkaline product. I am therefore very much inclined to suspect that in many cases a considerable portion of the ammonia which is produced in the destructive distillation of animal and vegetable substances actually proceeds from the destruction of the organic bases. This becomes the more probable when we consider that the organic bases have a more complex composition than ammonia, and that they are almost entirely converted into ammonia when passed once or twice over heated charcoal. In the same manner, when the organic alkaloids are heated in contact with potash or soda, or even when merely their aqueous solutions are boiled for a certain time, they always experience a partial decomposition, ammonia being constantly produced.—Liebig's *Annalen*, May 1849.

On a Product of Oxidation of Brucine. By M. Baumert.

As is well known, Gerhardt stated a few years ago that brucine, on treatment with strong nitric acid in the cold, furnished nitrous æther and a red non-volatile substance. Liebig, on the other hand, found that this substance differed in its properties from nitrous æther. Laurent subsequently confirmed the statements of Gerhardt, and gave the red substance the name of *cacotheline*. He expressed the decomposition of brucine by the following equation:—

$$C^{46}H^{26}N^{2}O^{8}+3(NO^{5},HO)=C^{42}H^{22}N^{4}O^{20}, \text{ cacotheline} + C^{4}H^{5}O,NO^{3}+2HO.$$

Subsequently Rosengarten examined this subject; he concluded from his experiments that the reaction is not so simple as appears from Laurent's equation.

The author has now followed out an observation previously described by Liebig, that a volatile substance can be obtained by other

oxidizing agents than nitric acid, for instance manganese. In this investigation, brucine, which had been crystallized from alcohol, was boiled half an hour with water in order to be sure of expelling the alcohol, and then distilled with manganese and dilute sulphuric acid from a retort. The best proportion between sulphuric acid, brucine and water is the following:—1 part crystallized brucine, 10 parts water and $4\frac{1}{2}$ parts hydrate of sulphuric acid. At first the heat must be very carefully raised, because otherwise the mass readily boils over. The tube terminating in the cooling apparatus must be pretty steep, in order to have as little water as possible in the distillate. Both condensing tube and receiver should be kept very cold. Oil-drops are seen to pass, especially at the commencement of the distillation; the operation is carried on as long as any inflammable vapour is evolved on the application of heat. The distillate can also be tested with nitrate of silver and a few drops of ammonia for the substance in question; however, the reaction of aldehyde is best seen with greater dilution. The distillate contains free formic acid. It is rectified over a very little chalk. It is now generally so free from water, that it burns on a glass rod. The author was not able to obtain the product perfectly free from water; treatment with anhydrous sulphate of copper, nitrate of lime, caustic lime, &c., was of no avail. Strong bases, as caustic lime, appeared to alter it on boiling; chloride of calcium did not separate the substance from its aqueous solution; the best plan therefore is to saturate the distillate, which has been rectified over chalk, with carbonate of potash, and to shake it well; two layers are then obtained; the upper one is perfectly limpid, and consists of the volatile substance; the lower one is a solution of carbonate of potash. The upper layer is removed with a pipette, without being heated with the lower one, which would render it yellow, and mixed with burnt alum, as it still contains carbonate of soda in solution. After several days no further disengagement of gas results on agitation. The neutral liquid is then rectified over chloride of calcium, which must not be in the least alkaline. Thus prepared, it is a clear liquid of aromatic odour, which burns with a blue flame and without residue.

In the analysis of this substance, the author obtained different results in four analyses. The substance for I. and II. had been rectified twice over chloride of calcium, that for III. and IV. only once:—

	I.	II.	III.	IV.
Carbon	33·94	33·75	31·08	31·21
Hydrogen	12·28	12·45	12·47	12·34
Oxygen.....	53·78	53·80	56·45	56·45

These results lead to no simple formula, and probably the two products were not free from water. To judge from the properties of this substance, it would appear to be an alcohol; the same results would have been obtained if the product examined had consisted of a mixture of pyroxylic spirit and water, as for instance—

	Wood-spirit and 9 p. c. Aq.	Wood-spirit and 17 p. c. Aq.
Carbon	34·2	31·1
Hydrogen	12·4	12·3
Oxygen	53·4	56·6

The view that the volatile substance is an alcohol is moreover supported by the following reaction:—When it is boiled with oxide of silver and barytic water then added, metallic silver is separated, and a soluble baryta salt is obtained, which on being evaporated to dryness and moistened with sulphuric acid, disengages a pungent odour belonging to some volatile acid.

Other oxidizing agents, as peroxide of mercury and peroxide of lead, further, chromate of potash and sulphuric acid, likewise produce this volatile substance from brucine.

With respect to the analytical results, they were subsequently repeated by Dr. Merck. The substance gave—

	Rectified once over CaCl.	Rectified twice over CaCl.	$C^2H^4O^2$.
Carbon	34·5	37·8	37·5
Hydrogen ..	12·2	12·4	12·5
Oxygen	53·3	49·8	50·0

Liebig's *Annalen*, June, p. 337.

On the Nature of the Lactic Acid in the Stomach.
By W. Heintz.

The author has isolated the lactic acid contained in the gastric juice of a female, and proved that it is the ordinary modification of the acid, and not the paralactic acid which occurs in muscular flesh.

A female who suffered from dyspepsia and took but little food, vomited from time to time a somewhat turbid liquid, in which only minute traces of the food occurred. This liquid had a strongly acid reaction; it was strained through linen, then filtered and evaporated in the water-bath to the consistence of a syrup. On the addition of alcohol, a large quantity of a tenacious brown substance was separated. The supernatant reddish-brown alcoholic liquid was separated, the alcohol distilled off, and the residue evaporated to a syrup. It was shaken for a considerable length of time with æther, the ætherial solution passed through a filter and set aside to evaporate. The residue was an acid syrup, which contained some acicular crystals that were not further examined.

The syrup which was not dissolved by the æther was mixed with a few drops of muriatic acid, and again agitated with æther. On evaporation, a further quantity of an acid syrup remained. The syrupy acid so obtained was now boiled with oxide of zinc and water, and the zinc salt, lactate of zinc, obtained by crystallization.

The air-dried salt lost up to 212° 18·14 per cent. of water. This agrees with the amount of water in ordinary lactic acid, which contains 3 atoms or 18·18 per cent., and readily parts with it at 212°; whilst paralactic acid contains only 2 atoms or 12·33 per cent., and loses it at 212° with far more difficulty.

The analysis of the dried zinc salt moreover yielded—

Carbon	29·74	6	29·62
Hydrogen	4·29	5	4·12
Oxygen	32·51	5	32·91
Oxide of zinc	33·46	1	33·35

It is quite evident, from the manner in which this lactic acid was procured, that a portion of it must be contained in the free state in the gastric juice, as it was immediately taken up by the æther. Another portion, on the other hand, may have been present in combination with bases, and have been set free by the addition of muriatic acid; yet it is known that lactic acid expels muriatic acid on evaporation with chlorides; and it is therefore certain that even a portion of the last quantity must have been in the free state in the stomach. In repeating any similar experiment, the author advises preparing the salt of lime instead of that of zinc; as it is quite possible with the latter, in the case of paralactic acid occurring at the same time, to overlook it, its zinc salt being more soluble than that of the ordinary lactic acid, whilst the lime salt is somewhat less soluble.—*Jenaische Ann. f. Physiol. u. Med.*, vol. i. p. 222.

Chemical Examination of the Bile of different Animals. *By* A. Strecker.

1. *Bile of Fish.*—The author obtained the bile of both fresh- and salt-water fish. It was collected at Rotterdam in the winter of 1847–48 by Dr. de Vry, evaporated with the necessary precautions in the water-bath, and in this state was transmitted to him. The fish from which the bile was procured consisted of the Turbot (*Pleuronectes maximus*, L.; *Rhombus maximus*, Cuv.), the Cod (*Gadus Morrhua*), the Pike (*Esox lucius*), and the Perch (*Perca fluviatilis*). The various biliary fluids of these fish were so much alike, that they were all treated as follows:—

They were dried in a water-bath, powdered, dissolved at a gentle heat in absolute alcohol, and set aside in a cold place. The liquid was then poured off from a somewhat considerable residue, which consisted of the mucus of the gall-bladder and some colouring matter. The alcoholic solution was of a much paler brown colour than is the case in ox-bile; a little æther precipitated almost all the colouring matter and a small portion of the other constituents; and after the separation of this precipitate, the principal part of the mass was precipitated by the addition of a large quantity of æther. The mixture of alcohol and æther was much concentrated in a water-bath, and again treated with æther, by which means a small portion of the principal biliary constituent was precipitated, which had remained in solution in the large amount of alcohol. On evaporation, the ætherial solution left crystals of cholesterine mixed with drops of oil, which were readily redissolved by æther. The precipitate and the ætherial solution had a strong fishy odour. The amorphous precipitate which was formed on the addition of the æther, be-

came crystalline when set aside and exposed to the air. Moreover, on covering the entire mass with æther, after standing for twenty-four hours, it became completely transformed into a mass of acicular crystals, which so closely resembled the sulphuretted constituent of the bile of the ox (Strecker's choleic acid), that there can be no doubt, as the following experiments prove, of their identity. This substance had a sweetish taste, becoming subsequently bitter, and was readily soluble in water; the solution had a scarcely perceptible alkaline reaction. On the addition of muriatic acid, or even concentrated sulphuric acid, in whatever proportion, no precipitate was thrown down, provided considerable heat was not produced. On boiling the solution which had been treated with these acids, an oleaginous or resinous substance separated in a short time. Neutral acetate of lead produced no precipitate; on the addition of basic acetate of lead, white flakes separated, which united, forming a plastery mass. On ebullition, the precipitate was completely dissolved, and on cooling reappeared in an unchanged state. After removing this precipitate, ammonia produced another precipitate in the solution which contained the excess of the lead salt; this was similar to the former. A considerable amount of the biliary matter remained in solution.

Nitrate of silver merely precipitated a small quantity of the coloured matter, which was at first thrown down by the æther; the second colourless precipitate yielded no precipitate with nitrate of silver. Perchloride of iron, added in very small quantity, produced a precipitate, which disappears when more is added. The aqueous solution of the biliary matter yields a flaky precipitate on the addition of solution of potash; this is readily soluble in pure water. When heated with sugar and sulphuric acid, the liquid exhibited the well-known violet colour.

For the sake of further testing this choleic acid, and comparing it with that from the bile of the ox, the precipitate thrown down by basic acetate of lead was kept in a state of ebullition with barytic water and hydrate of baryta for twelve hours. After separating the excess of baryta by carbonic acid, muriatic acid produced a resinous precipitate, which after having been moistened with æther, soon became hard and pulverizable. The liquid separated by filtration from the precipitate, after the removal of the baryta and muriatic acid by sulphuric acid and oxide of lead, left a comparatively large residue, in which only crystals of taurine could be detected, and which appeared to contain a very minute quantity only of glycocoll. When it was treated with alcohol, a trace only was obtained of a substance, which, when freed from muriatic acid by hydrated oxide of lead, dissolved the latter in small quantity; and even after the separation of the oxide of lead in solution, yielded a blue solution on ebullition with peroxide of copper, which was not precipitated by potash.

Cholalic acid could be shown to be a second product of decomposition of the choleic acid from the bile of the fish. The precipitate produced by muriatic acid was readily soluble in alcohol, and deposited crystallized cholalic acid in the form of tetrahedra. The

analysis I. is that obtained from the cholalic acid of the bile of *Gadus Morrhua*, dried at 284° F.; II. is that of the acid of the bile of *Pleuronectes maximus*, dried at 266° F.:—

	I.	II.		
Carbon.....	70·1	70·8	48	70·6
Hydrogen	9·9	9·8	40	9·8
Oxygen	..	..	10	19·6
				100·0

On drying the substance found in analysis I., 10·4 per cent. of water were obtained; the formula of cholalic acid, $C^{48}\ H^{40}\ O^{10} + 5HO$, requires 9·9 per cent. The atomic weight of this acid was determined from the barytic salt; the acid was dissolved in barytic water, and the excess of baryta separated by carbonic acid, the current of which should not be continued longer than is requisite, otherwise the salt becomes decomposed; it was then dried at 212° F. The substance was procured from the *Gadus Morrhua*, and yielded—

	Equiv.	Calculated.	Found.
Carbon	48	60·6	60·2
Hydrogen	39	8·2	8·2
Oxygen	9	15·1	
Baryta.....	1	16·1	16·4
		100·0	

The products of decomposition of the bile mentioned above show that it consists almost entirely of choleates. The bases are several, and cannot be accurately determined on account of the small quantity of ash which the bile yields. But the bile may be readily converted into a salt with a single base by freeing it from the other admixtures by alcohol and æther, dissolving it in the smallest quantity of water possible, and adding a concentrated solution of potash in the cold. Almost the whole of the organic matter then separates in combination with potash, in the form of flakes, which may be collected on a filter, and washed with solution of potash. The pressed residue is then dissolved in absolute alcohol, and the excess of potash removed by a current of dry carbonic acid; the choleate of potash remaining in solution may be obtained in a solid state by evaporation, or what is better, the addition of æther. By this process the bile of the *Pleuronectes maximus* was converted into a potash salt, yielding when dried at 248° F.—

Carbon	56·8	52 =	312·0	56·4
Hydrogen	8·1	44	44·0	8·0
Nitrogen	..	1	14·0	
Oxygen	..	13	104·0	
Sulphur.....	..	2	32·0	
KO.....	8·8	1	47·1	8·5
			553·1	

In the case of the bile of the other kinds of fish, the author did not adopt this conversion into a potash salt, but merely precipitated

the various kinds of bile from the alcoholic solution by æther, dried them at 248° to 266° F., and analysed them. The results are the results:—

	Gadus Morrhua.	*Pleuronectes maximus.*	*Esox lucius.*	*Perca fluviatilis.*
Carbon	56·10	56·20	59·40	..
Hydrogen	8·10	8·00	8·30	..
Nitrogen	..	..	..	..
Oxygen	..	..	..	..
Sulphur	5·66	5·91	5·77	5·99
Ash	12·60	14·60	11·80	11·40
Sulphates	14·50	17·10	13·90	14·10

On comparing the subjoined theoretical calculations of the composition of the cholcate of potash and soda, we find that the cholcate of potash is the predominating constituent of the two first kinds of bile; whilst the two last contain proportionately more soda, which in the bile of the *Esox lucius* must partly be combined with cholic acid. The calculated composition of these salts is as follows:—

	Cholcate of Potash.	Cholcate of Soda.	Cholate of Potash.	Cholate of Soda.
Carbon	56·4	58·1	62·0	64·1
Hydrogen	8·0	8·2	8·3	8·6
Nitrogen	2·5	2·6	2·8	2·9
Oxygen	18·8	19·3	17·5	18·0
Sulphur	5·8	6·0		
Base	8·5	5·8	9·4	6·4
	100·0	100·0	100·0	100·0

These salts leave the following quantities of ash after having been moistened with sulphuric acid (in the same order):—

15·7 13·2 17·3 14·6

It is a remarkable circumstance, that the bile of marine fish living in sea water, which is so abundant in soda, principally contains potash; whilst in the bile of the ox, the food of which abounds to such an extent in potash, the ash consists of a large quantity of soda with mere traces of potash.

2. *Bile of the Dog.*—The properties of the bile of the dog exactly resemble those of the kinds of bile described above. On evaporating it, and dissolving the residue in alcohol, æther precipitates flakes of a slightly coloured substance, which gradually become crystalline. If the liquid be decanted from the precipitated substance, and be replaced by æther, the conversion into crystals takes place more rapidly.

On the decomposition of this substance, the author again obtained cholalic acid and taurine, with which no trace of glycocoll appeared to be mixed; it agreed in all its properties with that from the cholcate of soda. The properties of the bile of the dog appear to be independent of the food of the animal; for the bile of a dog fed upon flesh was not found to differ from that of one which had consumed

a vegetable diet. On the analysis of the purified bile of the dog, dried at 248° F., the author obtained results which almost exactly agree with those of Schlieper's analysis of the bile of the serpent (*Boa anaconda*). The results of both express pretty accurately the composition of the choleate of soda, as shown by the following comparison:—

	Equivalents.	Calculated.	Dog's bile.	Serpent's bile.
Carbon	52	58·1	58·2	58·1
Hydrogen	44	8·2	8·5	8·5
Nitrogen	1	2·6	..	3·4
Oxygen	13	19·3		
Sulphur	2	6·0	5·9	6·2
Soda	1	5·8	5·8	11·5 (ash)
		100·0		

3. *Bile of the Sheep.*—The products of the decomposition of this bile show that, like the preceding kinds of bile, it consists of a mixture of a large quantity of choleate of soda with a little cholate; it yielded cholalic acid, taurine and glycocoll. It is of a much darker colour than the preceding; and its colouring matter appears to be identical with that of the bile of the ox. As the bile had been previously analysed by Bensch, who found it to contain from 5·7 to 5·3 per cent. of sulphur, the author did not make any further determinations.

[To be continued.]

On the supposed Combination of Nitrogen with Oxide of Lead.
By K. Stammer.

This compound, which was described some time back by M. Bley, has been examined by the author, who found that the gas given off was merely atmospheric air proceeding from the apparatus, which could not be perfectly freed from it, and some oxygen from the lead compound, which was no compound of nitrogen with oxide of lead, but a mixture of oxide of lead with minium. The gas was collected over a saturated solution of chloride of sodium, the carbonic acid removed by agitation with hydrate of potash, and the remaining gas, which occupied but very little space, left for a long time with phosphorus in a graduated tube. This absorbed three-elevenths of the volume; the remainder was nitrogen.—Liebig's *Annalen*, June 1849.

CHEMICAL PREPARATIONS.

Observations on the Preparation of Mineral Kermes.
By T. Derouen.

The author has published an extensive treatise on kermes, its preparation, and especially its production in a uniform state. It

contains no analyses to ascertain the composition of this substance, which has been already so frequently examined. Its object is rather to discover the circumstances under which a kermes may be obtained with certainty, free from oxide of antimony and alkaline sulphuret. The first admixture can now, as Rose has shown, be avoided; but with respect to the latter, the author is of opinion that none of the officinal kermes up to the present time has been free from it.

The methods recommended for the preparation of kermes are, including the older ones, for instance those of Lemerey and La Ligerie, essentially of three kinds:—1st, sulphuret of antimony is boiled with carbonate of potash or soda; 2nd, caustic alkali is substituted for the carbonate in 1; 3rd, a mixture of sulphuret of antimony and carbonated alkali is fused at a red heat, and the fused mass treated with boiling water. The author prepared kermes—

A. *According to the recipe of Cluzel.*—20 grms. of finely-pulverized sulphuret of antimony and 200 grms. of carbonate of soda were boiled with 4 quarts of water for two hours in a cast-iron vessel. 9·5 grms. of kermes of a beautiful velvety colour were obtained.

B. *According to the recipe of Beaumé.*—30 grms. sulphuret of antimony were fused with 60 grms. carbonate of potash and 2 grms. of sulphur. Of the mass so obtained, 47 grms., which contain just as much sulphate of antimony as the preceding mixture, were boiled for two hours with 4 quarts of water. 18·10 grms. kermes were obtained, but of a less beautiful colour than according to Cluzel's method.

C. *According to Berzelius.*—30 grms. of sulphuret of antimony were fused with 80 grms. of carbonate of potash, and 56 grms. of the mass obtained exhausted with boiling water. 11 grms. kermes, of a very beautiful but not velvety appearance, were obtained.

D. *According to Thierry.*—30 grms. sulphuret of antimony and 10 grms. dry carbonate of soda were fused together, and two-thirds of it boiled for two hours with 4 quarts of water which contained 4 grms. carbonate of potash. The precipitate which was deposited had a bad colour, and was in such a fine state of division that it passed through the filter. Only 2·05 grms. could be collected.

E. *According to Liance.*—This process appears to be derived from some old Pharmacopœia, and consists of two operations:—

I. 500 grms. of cow-hair and 1 kilogramme of potash are placed in alternate layers in a crucible, which is then covered, and the mass fused until no more gas is disengaged.

II. 15 kilogrms. of sulphuret of antimony, 8 kilogrms. carbonate of potash and 50 litres of river-water are then taken, and the sulphuret of antimony broken into long pieces and boiled with the 50 litres of water in an iron pan. 2 kilogrms. of potash are then added to it, and afterwards $\frac{1}{4}$ of the preparation I. It is then boiled for an hour, filtered into a hot dish, and the liquid poured whilst hot into two warm cylindrical vessels, which are well covered and left to stand till the following day. The pan is again filled with water and 1 kilogrm. of carbonate of potash, and the second fourth of the preparation I. added. The same operations have to be gone through as above, only that the liquid obtained is poured into two fresh cy-

lindrical vessels. This is repeated until all the four-fourths of the preparation I. are consumed. We have now eight vessels. The alkaline liquid is poured from the two first upon the sulphuret of antimony in the pan, which is again filled with water, and the operation previously described repeated. The same is done with the other vessels in succession. This can be continued for a month if the sulphuret of antimony is well stirred, and 1 kilogrm. of potash is added about every six days to each liquid of the four series. The deposits from the different vessels are collected daily, and thrown upon a linen strainer, which is covered with bibulous paper. They are washed with hot water, and dried with exclusion of the light between 59° and 64°. Kermes which has been prepared according to this method is insofar remarkable as part of that which is met with in the commerce of Paris is obtained in this manner. Samples which the author prepared according to the above directions were not so beautiful in colour as that obtained according to Cluzel's process; moreover, the produce was much smaller. These samples however exhibited no difference on comparison with kermes prepared by M. Liance himself. That chemist asserts that kermes prepared according to his directions is of constant composition; but this is contradicted by the fact that he himself furnishes a kermes No. I. and II., and likewise that more or less oxide of antimony must be precipitated in proportion to the time the precipitate was left in contact with the liquid.

With regard to the employment of cow-hair in this process, this can only produce a quantity of caustic potash, sulphuret and cyanide of potassium. The author has examined the product, and found that so little cyanide of potassium is formed, that the whole effect must be ascribed to the sulphuret of potassium alone; and consequently the hair may be replaced by an addition of sulphur. From an analysis of cow-hair, it was found that 2 grms. contained 0·064 grm. sulphur. If we calculate accordingly the quantity of sulphur corresponding to the weight of cow-hair, the disagreeable operation of fusing it with potash can be avoided. A kermes is obtained which cannot be distinguished from that prepared strictly according to the directions of M. Liance.

Under all circumstances where kermes is produced, it is always formed by the reciprocal action of sulphuret of antimony and an alkali; in this operation there is principally formed hydrated sulphuret of antimony; but at the same time, as a secondary product, oxide of antimony; and a certain amount of alkaline sulphuret always adheres to the sulphuret of antimony, which cannot be removed by washing, whilst the oxide of antimony is held in solution by a large excess of potash.

According to the author's view, kermes is formed in this manner:—On the first action of the sulphuret of antimony upon the carbonate of potash or soda or on caustic alkali, a sulphuret of the alkali is formed, which then again unites with the sulphuret of antimony forming a sulpho-salt, SbS^3, KS or SbS^3, NaS, in which the sulphuret of antimony acts the part of an acid. This salt, which is very

soluble in water, is decomposed by the weakest acids, even by the carbonic acid of the atmosphere. It converts the double sulpho-salt into carbonate and hydrated sulphuret of antimony. Carbonic acid however expels only half of the sulphur or of the sulphuretted hydrogen which the monosulphurets or the hydrosulphates contain; and it is owing to this cause that in all the above methods so little kermes is obtained, by far the greater portion being left in the mother-ley.

The author now prepared the sulpho-salt directly by boiling for two hours 20 grms. of sulphuret of antimony with a solution of the monosulphuret of sodium, prepared with 40 grms. of caustic soda in 1 litre of water. The liquid, on gradually cooling, left not a trace of a precipitate. Into this solution sulphuretted hydrogen was passed, when a bulky precipitate, weighing 4·5 grms., was obtained.

In a perfectly similar experiment with monosulphuret of potassium, employing a quantity of potash equivalent to the above amount of soda (60), there were obtained 5·47 grms. kermes.

The author thence concludes that in the preparation of kermes a double sulphuret of antimony and an alkali are first produced, which then, by further decomposition in the air, furnishes carbonated alkali and sulphuret of antimony. To demonstrate this by further experiments, 20 grms. of sulphuret of antimony were boiled for a whole day with a solution of hydrosulphuret of potassium, KS, HS, prepared with 60 grms. of potash, replacing every now and then the evaporated water. Not a trace of kermes was formed, and the sulphuret of antimony did not decrease in weight. It is evident therefore that the sulphuret of antimony, SbS^3, really acts the part of an acid, since it combines with KS or NaS, but not with the hydrosulphurets KS, HS or NaS, HS, in which sulpho-salts the sulphuretted hydrogen occupies the place of the sulphuret of antimony, and is a more strongly negative body, since the sulphuret of antimony may be separated by it from the combinations KS, SbS^3 or NaS, SbS^3.

The kermes prepared with the alkaline monosulphurets does not possess a beautiful colour; it may easily be obtained free from oxide of antimony when the alkaline sulphuret is correctly prepared; but it is difficult to free it from sulphuret of potassium or sulphuret of sodium, which adhere tenaciously to it. The author however succeeded in procuring a kermes containing scarcely $\frac{1}{2}$ per cent. of alkali by the following process:—The kermes, prepared as above directed with sulphuret of sodium, was frequently washed with hot water, and then transferred to a tall displacement apparatus. A mixture of equal parts of boiling alcohol and water was poured upon it, the upper part of the apparatus closed with a cork, and a current of sulphuretted hydrogen passed for a quarter of an hour into the mixture. As soon as the liquid had drained off, boiling alcohol was poured upon it, with the precaution that no air could enter the apparatus. This operation was repeated for several hours, when the apparatus was set aside for the kermes to deposit. It was washed and dried.

This kermes was of a chestnut-brown colour, had no velvety ap-

pearance, appeared under the microscope to be free from crystals of oxide of antimony, and furnished, after treatment with muriatic acid, a liquid which deposited mere traces of chloride of sodium.

According to H. Rose, kermes, when free from oxide of antimony, furnishes a black mass when fused in a current of carbonic acid, the powder of which is likewise black. Kermes containing oxide of antimony may also be black after fusion, but the powder is brown or red. The different preparations treated of in this paper all fused to a more or less black mass; but that prepared according to Beaumé and Thierry gave a brown powder; that according to Berzelius a brown powder with a reddish tint; that according to Cluzel a blackish-brown powder; that according to Liance a very readily fusible mass and red powder; and that prepared according to the author's method a beautiful black powder. It is evident therefore that—

1. Kermes is obtained according to Cluzel's method of a beautiful colour and tolerably pure. In the last respect it is only inferior to that prepared with monosulphuret.

2. A kermes with a colour nearly as beautiful is obtained according to the methods of Beaumé and Berzelius, but it contains a large amount of oxide of antimony: this method is otherwise the quickest for preparing kermes.

3. The preparation by means of monosulphurets furnishes the purest kermes; but it cannot be carried out on a great scale for commercial purposes.

4. Under all circumstances the moist way must be adopted and a large excess of alkali used, in order to obtain a kermes free from oxide of antimony.

5. Those pharmaceutists who adopt the process of M. Liance may substitute a corresponding amount of sulphur for the cow-hair.

6. In all cases where kermes is formed, there must first be produced a double sulphuret of alkali and antimony, which is decomposed by weak acids, for instance the carbonic acid of the atmosphere into carbonated alkali and kermes. The various kinds of kermes met with in commerce have all a very variable composition.—*Journ. de Pharm. et de Chim.*, xv. p. 5.

On the Adulteration of Kermes. By M. Bussy.

In the 'Journal de Pharmacie' for October the author draws attention to the fact, that during this year's visitation the kermes was found at a large number of chemists and druggists in Paris to consist almost entirely of peroxide of iron. This adulteration is easily detected. About a gramme of the suspected kermes is heated in a small flask with 5 or 6 cubic centimetres of pure concentrated hydrochloric acid. Pure kermes dissolves with a considerable disengagement of sulphuretted hydrogen; the liquid is colourless, milky, and deposits a little sulphur; it is heated to boiling, in order to expel the sulphuretted hydrogen, and filtered; the liquid should pass

through colourless. If the kermes contain peroxide of iron, the proportion of sulphuretted hydrogen is less considerable, sometimes scarcely perceptible. The deposit of sulphur is very copious, and the filtered liquid, instead of being colourless, is of a more or less deep yellow according to the amount of iron it contains. In all cases the liquid is mixed with a little of a concentrated solution of tartaric acid to prevent the precipitation of antimony, and then diluted with water; a little prussiate of potash is then added, which instantly produces a very copious blue precipitate if the kermes contain iron.

Observations on the Butter of Antimony. By A. Larocque.

Sérullas has shown, in his treatise on the pharmaceutical preparations of antimony, that all these preparations contain arsenic, excepting tartar-emetic and the protochloride of antimony. It must therefore be interesting to pharmaceutists to learn how it is that these two combinations are obtained free from arsenic. The author first followed the directions of the French Codex for the preparation of the butter of antimony.

To prepare this compound, sulphuret of antimony containing sulphuret of arsenic is usually employed. As soon as this is treated at a gentle heat with an excess of muriatic acid, sulphuretted hydrogen escapes, and a solution is obtained in which protochloride of antimony and a small quantity of sulphuret of arsenic are contained. This solution furnishes, on evaporation and distillation, the butter of antimony. In this distillation we first observe that muriatic acid with very little protochloride of antimony pass over; as soon as the temperature rises, the retort becomes coated with an orange-coloured precipitate, whilst as yet but little butter of antimony passes over. Soon after this the concussions which previously occurred cease, and the yellow deposit no longer increases. The distillation of the protochloride of antimony now proceeds without further hindrance.

We observe therefore in the preparation of the butter of antimony two phases. During the first, muriatic acid passes over, and as this disappears the sulphuret of arsenic held in solution in the protochloride of antimony by the excess of muriatic acid separates. The distillation of the butter of antimony really takes place only during the second period. When therefore the receiver is changed at the proper time, the preparation is obtained perfectly free from arsenic.

It results from this behaviour, that with butter of antimony prepared in the above manner, powder of Algaroth may be obtained perfectly free from arsenic, which is not the case when the chloride of antimony used for this purpose is prepared by treating sulphuret of antimony with nitric acid, and dissolving the oxide produced in muriatic acid.—*Journ. de Pharm.*, xv. p. 161.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Absorption of Saline Substances by Charcoal.
By M. Esprit.

A very remarkable property of carbon is the precipitation of certain metallic salts from their solution in water by animal charcoal. This curious property, the discovery of which is attributed to M. Payen, appears to have been previously noticed by Schaub*. Subsequently M. Payen announced that charcoal removed lime and salts of lime from their solution in water. A few years later Dubrunfaut confirmed the observations of M. Payen, and announced as a general principle that the carbon saturated the alkalies and appropriated them; that it, moreover, appropriated the salts, and especially the calcareous salts which occur in the juice of the beet-root after defecation; and he insisted on the advantages which this two-fold property presented in the manufacture of beet-root sugar. Graham, whose experiments date from 1829, examined principally the action of charcoal upon the acetate and nitrate of lead, arsenious acid, nitrate of silver, sulphate of copper and ammoniacal sulphate of copper, hydrate of lead dissolved in potash, solution of iodine, Labarraque's solution, chloride of lime, and liquid chlorine. He states that, however large the quantity of charcoal employed, he was never able to precipitate arsenious acid and sulphate of copper. The contrary was the case with all the other salts. M. Lassaigne found that charcoal, placed in contact with iodide of starch and with a solution of iodine, removes the iodine from the liquid. M. Dupasquier observed that vegetable charcoal absorbs quickly and even in considerable quantity the alkaline sulphurets. I have repeated this experiment comparatively with vegetable and animal charcoal, and have found that it requires nearly three and a half times more of the former than of the latter to obtain the same result.

In 1845, M. Chevalier published in the 'Annales d'Hygiène,' that the acetate and nitrate of lead in solution in water, wine or vinegar, might be removed from these liquids by means of charcoal, with or without the assistance of heat. He was led to believe that this new property would furnish a ready and easy means of removing from some orange-flower waters, which had been kept in badly-tinned vessels, the lead salts they might have dissolved, without depriving

* Annales de Chimie, xlix. p. 62.

the waters of their odour. The experiments which he made on this subject perfectly confirmed his suppositions. M. Chevalier also observes very correctly, that this property of charcoal of combining with the metallic oxides may frequently have been the source of error in chemico-legal inquiries.

This question has also been examined by M. Girardin, who found that not only the majority of salts, but even most mineral substances, were removed from solution by animal charcoal; a property which he turned to excellent account in depriving water from newly-constructed reservoirs of a disagreeable flavour, which renders its use for a long time impossible, owing to the lime which it removes from the walls.

I have still to notice the experiments made by Messrs. Garrod and Weppen; but the results obtained by these two chemists are so little in accordance, and differ so much from those published by Prof. Graham, that I have considered it indispensable to repeat their experiments and in different ways, in order to ascertain whether the difference of the results at which they arrived should not be principally attributed to the varied conditions under which they operated. All my experiments were made with three distinct kinds of charcoal:—

1. With animal black, freed from the carbonate of lime which it contained, but still retaining the phosphate.

2. With animal charcoal, digested with hydrochloric acid, and washed with distilled water until what passed through no longer furnished a precipitate with oxalate of ammonia or with nitrate of silver: a considerable quantity of this charcoal, on calcination in a platinum crucible, left but an insignificant residue of silica.

3. With blood-charcoal, calcined twice with a mixture of carbonate of soda and potash, and then washed with distilled water until it no longer furnished a trace of alkaline cyanide.

I tried the action of these charcoals in three different manners:—1st, by mixing a known weight of charcoal with a certain quantity of saline solution, and setting the mixture aside; 2nd, by boiling a known weight of charcoal with the saline solution; 3rd, by filtering the metallic solution through a layer of charcoal placed in the neck of a retort, and acting thus by way of displacement.

Of these different methods, the third is that which appeared to be the most advantageous, only it has the inconvenience of being rather tedious and also somewhat capricious. To obtain a satisfactory result, it is requisite that the filtration should proceed slowly, otherwise some of the liquid passes without being decomposed. The second process is undoubtedly quicker, but it always appeared to require a greater proportion of charcoal for the same quantity of salt.

The solutions of metallic salts upon which I operated are the following:—The acetate, sulphate and nitrate of copper; the acetate, sulphate, chloride of zinc and oxide of zinc dissolved in ammonia; acetate and nitrate of lead; acetate and sulphate of iron; tartar-emetic; the nitrate and sulphate of silver, and the chloride dissolved

in ammonia; corrosive sublimate; nitrate of cobalt; sulphate of cadmium; arsenious acid; nitrate and muriate of baryta; and the sulphates of soda, potash and magnesia.

With the exception of the three alkaline sulphates, the nitrate of copper and arsenious acid, which appear to be absorbed only within exceedingly restricted limits, all the other salts were absorbed with greater or less energy.

5 parts of blood-charcoal calcined with potash sufficed to precipitate entirely the following salts:—Acetate and nitrate of lead; ammoniacal sulphate of copper; the sulphate and nitrate of silver, and the chloride dissolved in ammonia; the chloride of zinc, and oxide of zinc dissolved in potash.

20 parts of charcoal are required to precipitate the sulphate and acetate of copper, corrosive sublimate, nitrate of cobalt, sulphate of cadmium, tartar-emetic, sulphate of zinc, and chloride of barium.

The precipitation however is only perfect for the first five salts; and it appeared very difficult, even by increasing the proportion of charcoal, to remove entirely the last traces of the four others, which are it is true sometimes very minute, but can still be detected. Thus the quantity of tartar-emetic which is not absorbed is so small, that its presence is no longer indicated by sulphuretted hydrogen; but it may still be discovered with Marsh's apparatus.

The proportions of charcoal above indicated are only strictly accurate for the salts of copper; for the others they are only approximative; but they nevertheless approach very closely the true limits. The following is the plan which I followed to ascertain the quantity of charcoal necessary for the absorption of the sulphate and acetate of copper. I dissolved in 8 grms. of acid diluted with water 2 grms. of oxide of copper obtained by calcining the nitrate, evaporated the solution to dryness, then redissolved the salt in 100 grms. of distilled water, and placed the solution in a wide-mouthed bottle with a ground stopper. I then poured some ammonia into it until the precipitate which formed at first had redissolved and the liquid had become perfectly clear; the bottle was finally filled with boiled distilled water, and a bright slip of copper, the weight of which was known, inserted. In the course of five days the experiment was completed, and the solution had become perfectly colourless; the slip of copper was then removed, washed, wiped dry with care and weighed. It had lost 1·4 of its weight. This experiment, repeated several times in the same manner, furnished the same result.

As the oxide of copper contains precisely half the quantity of copper contained in the subtoxide, it proved that my primitive solution contained 1·4 copper. If, therefore, after having been filtered through charcoal, it contained less copper, that must have held it back. A solution of copper was therefore prepared like the preceding, and transferred into the displacement-apparatus with 10 grms. of animal charcoal. As soon as the operation was finished, I washed the charcoal with a little distilled water, added this wash-water to the filtered liquid, supersaturated it with ammonia, &c. As soon as the decoloration was complete, I removed the slip of copper to weigh

it. It had lost only 0·75 of its weight; the charcoal had therefore retained 0·65 copper, or nearly half of what the solution contained. I repeated the experiment, and obtained 0·70, and a third time 0·75.

With regard to the alkaline sulphates, they always appeared to be absorbed in very minute proportions; for I was not only able to detect their presence readily by means of reagents, but sometimes even from the bitter taste of the solution, especially when the liquid had been slightly concentrated.

I next proceeded to ascertain the quantity of arsenious acid which animal charcoal is capable of absorbing. Prof. Graham had asserted that no absorption occurs; Dr. Garrod states, on the contrary, that it is so perfect and quick, that he did not fear to recommend charcoal powder as a far better antidote to arsenic than the hydrated sesquioxide of iron. I adopted the following plan for testing the correctness of these assertions. After having found that, even on employing very considerable quantities of charcoal, arsenious acid was constantly detected in the filtered liquid, I endeavoured to ascertain whether any had been absorbed. For this purpose I dissolved 10 grms. of arsenious acid in a litre of distilled water; I then took 10 cub. centim. of this solution, to which I added 10 cub. centim. ClH, with 100 cub. centim. distilled water, and which served to determine the strength of a solution of permanganate of potash, intended for estimating the arsenic according to M. Bussy's process. Having determined the strength of the normal solution, I poured 100 cub. centim. of the solution of arsenious acid over different quantities of charcoal; and when the filtration was finished, I washed the charcoal with a little distilled water, so as to reobtain 100 cub. centim. Of this I took the first time 10 cub. centim., and added to them 5 cub. centim. ClH and 100 cub. centim. distilled water. I then added with precaution the permanganate of potash. The following results were obtained with blood-charcoal:—

10 grms. of charcoal	absorbed	0·2	AsO^3
20 ...	...	0·3	...
40 ...	...	0·4	...

Upon boiling the arsenical solution with the charcoal, the results were somewhat different:—

10 grms. of charcoal	absorbed	0·3	AsO^3
20 ...	...	0·5	...
40 ...	...	0·7	...

A still more difficult question remained to be solved—How does the charcoal act under these circumstances? Is there any reduction? or is it merely a simple phænomenon of mechanical absorption, as in dyeing? I believe the latter occurs most frequently; but would except the salts of silver, and all those metals the oxides of which are readily reduced. I would also except the salts of lead, which appear to be converted, for the greater part at least, into the state of carbonate. This is partly indicated by the white deposit which covers the surface, and even penetrates pretty far into the interior

of the layer of charcoal through which a solution of a lead salt has been filtered.

There is likewise frequently a change in the composition of the salt; sometimes a subsalt is formed, and free acid is found in the liquid; sometimes a subsalt is formed, which is retained by the charcoal, whilst a very acid salt passes through in the liquid: this is what undoubtedly happens with the sulphate of iron and the sulphate of zinc, which renders it almost impossible to precipitate the last portions of these salts; frequently, however, it is merely a simple absorption. Thus if 1 grm. of acetate of copper is dissolved in 100 grms. of distilled water, the liquid acidulated with one drop of acetic acid, and the solution poured over 20 grms. of well-washed animal charcoal placed in the neck of a retort, not a trace of copper will be found in the liquid if the filtration proceeds regularly, and not too rapidly; the charcoal may even be washed with 100 grms. of distilled water, the liquids united and concentrated, and still no copper be indicated by reagents. But if the charcoal be triturated in a glass mortar with water, so as to isolate the molecules and thus to assist the solvent action of the water, it removes some of the salt which the charcoal had retained, and its presence is now readily detected.

The following experiment will serve still better to establish my view. 1 grm. of corrosive sublimate was dissolved in 100 grms. of distilled water, and the solution filtered through 20 grms. of well-washed animal charcoal. At the end of thirty-six hours half the liquid had passed through; the presence of a salt of mercury was sought for in it with potash, sulphuret of ammonium, and iodide of potassium, but no change was produced by these reagents.

At the end of twice forty-eight hours the whole of the liquid had filtered, the charcoal was washed with distilled water, and the same tests applied again with the same result. But perhaps the bichloride of mercury had undergone some alteration in its composition in contact with the charcoal; perhaps it had been reduced to the state of protochloride, and consequently become insoluble. Such is the opinion of Weppen; which, however, does not agree with the observation made by Fourcroy, who in his *Système des Connaissances Chimiques*, states in a positive manner that the charcoal has no action upon corrosive sublimate, either with or without the assistance of heat.

The following experiment will, I think, decide the question. The charcoal which had taken up the corrosive sublimate was washed with a mixture of alcohol and æther, which quickly dissolved the mercurial salt in the state of corrosive sublimate; and in such quantity, that it became possible to trace, with a tube dipped in it, characters of a brilliant red upon a plate of porcelain which had been moistened with iodide of potassium. The ætherial solution left on evaporation a white powder, which, dissolved in distilled water, fursinhed with potash an orange precipitate; with hydrosulphate of ammonia, a white precipitate, which soon turned black; and lastly, with iodide of potassium a red precipitate. It appears evident,

therefore, that there was no reduction, but a simple phænomenon of absorption, analogous to what takes place in the decoloration of indigo, where the charcoal can be deprived of the colouring matter which it had combined with by an alkaline solution; that is to say, by a substance having a greater affinity for it than the charcoal. The same occurs when the affinity of the charcoal for the corrosive sublimate is overcome by the stronger affinity of the æther or alcohol; the salt can then be redissolved; or, as was the case with the acetate of copper, when the affinity of the charcoal was weakened by mechanical means by isolating the molecules, the water is able to retake up the salt which it had previously abandoned.

This explanation which I venture to propose will, I think, not appear surprising, for we are prepared for it by the behaviour of charcoal under other circumstances. The way in which it removes lime and calcareous salts is a phænomenon of pure absorption; there can have been no reduction in such a case. Messrs. Bussy and Payen have satisfactorily demonstrated that there is no chemical action in the decoloration of liquids; and the way in which it combines with the bitter principles of vegetables can only be explained by a peculiar affinity.

The attention of chemists was called to this new and curious property by Mr. Warington. It had, it is true, already been pointed out by M. Duburgua, who had long before stated that tincture of gentian was entirely deprived of its bitterness by being filtered through charcoal; by M. Chevalier in 1826; by M. Holph in 1831; and M. Rhighini six or seven years back, who advised the use of charcoal as an excellent plan for obtaining the bitter principle of wormwood.

Notwithstanding all these experiments, the property which this substance possesses of combining with certain organic principles was nearly forgotten, when, in 1845, Mr. Warington again called the attention of chemists to it. Having been requested by a brewer to find a convenient and easy method for decolorizing large quantities of brown ale, so as to give it the appearance of pale ale, he immediately thought of charcoal. The beer was decolorized, but had become perfectly insipid. Little prepared for such a result, Mr. Warington repeated his experiments upon different kinds of beer, and lastly upon infusions of hops, wormwood, decoctions of gentian, nux vomica, and even aloes. All these substances lost their bitter taste except nux vomica.

M. Weppen somewhat extended these experiments, and succeeded in causing the bitterness of decoctions of columbo, quassia, cascarilla, and buckbean to disappear.

At the same period, M. Chevalier announced that the salts furnished by organic substances are removed more or less readily and entirely by treatment with charcoal and the assistance of heat; that in some cases the absorbing property of charcoal might be turned to account for isolating the poisonous substances held in solution.

Subsequently, Dr. Garrod proposed charcoal as a certain antidote for all the vegetable alkalies.

Lastly, in a very recent communication, M. Lebourdais* has employed charcoal to obtain certain vegetable alkalies: thus, after having deprived a decoction of ilex of its bitterness, he was able, by treating the dried charcoal with boiling alcohol, to redissolve the bitter principle; and then, by distilling to a syrupy consistence to remove the greater proportion of the alcohol, and evaporating to dryness, to obtain an amorphous neutral substance, to which he gave the name of *ilicine*. By treating infusions of *Scilla*, flowers of *Arnica*, a decoction of the root of Colombo and of Colocynth in the same manner, M. Lebourdais obtained what he has called Scillitine, Arnicine, Columbine, and Colocynthine.

I have also deprived, by the same means, aqueous solutions of strychnine, sulphate of quinine, decoction of box, root of *Rumex patientia*, of *Simaruba*, the tinctures of columbo, sarsaparilla, dulcamara, cinchona and rhubarb, &c. of their bitter taste.

The tinctures of benzoin, kino, and gamboge, were deprived of their resinous principle to such an extent, as to be no longer rendered turbid by the addition of water.

I was desirous of ascertaining whether any other porous substances possessed this property of charcoal. I tried pumice-stone, and obtained no good result; but by means of platinum-black I have succeeded in depriving of their taste and colour a number of tinctures; the tincture of columbo succeeded best; 2 grms. of platinum entirely deprived 8 grms. of tincture of taste, but at the same time there is produced a certain quantity of aldehyde and acetic acid. Unfortunately, the action of platinum black appears to be quickly exhausted; and it does not appear to me to stand in any relation to the force which might be expected from its excessive porosity and extreme division; I am therefore led to believe that the property possessed by charcoal is not solely due to its porosity, but that it is also owing to some peculiar affinity.—*Journ. de Pharm.* Sept. and Oct. 1849.

Chemical Examination of the Bile of different Animals.
By A. Strecker.

[Continued from p. 431.]

4. *Bile of the Pig.*—The author has shown in his earlier investigations, which were made conjointly with Gundelach†, that the greater part of the bile of the pig consists of an alkaline hyocholate. The hyocholic acid was found to differ essentially from the acids of the bile of the ox. It is insoluble in water; forms with lime and baryta salts which are insoluble, or very difficultly soluble in water; its alkaline salts are almost entirely separated from the aqueous solution by chloride of sodium, muriate of ammonia, or alkaline sulphates. By means of the latter reaction, the acid and its salts were previously obtained in a state of purity, and analysis led to the following formula for all the salts, $C^{54}\,H^{43}\,NO^{10} + MO$, whilst the com-

* Chem. Gaz., vol. vi. p. 442. † Ibid. p. 138.

position of the acid corresponded to $C^{54}H^{43}NO^{10}$. The composition of the whole of that portion of the bile of the pig which is soluble in alcohol and insoluble in æther, and which amounted to about 75 per cent. of the dry residue of the bile, was found to differ somewhat from this; a small quantity of sulphur (0·47 per cent.) could also be detected in this portion.

This quantity of sulphur was then regarded as not essential, probably as arising from sulphates; because at that time the bile was still considered to consist of a single substance (biline on the one hand, and choleate of soda on the other). But after Strecker's investigations had shown that the various kinds of bile generally contain two alkaline salts, the salt of one acid containing sulphur, and that of another free from sulphur, we are justified in concluding in this case also, that this quantity of sulphur must belong to a small quantity of an acid corresponding to choleic acid. The author pointed this out a year and a half ago, and very shortly afterwards showed that taurine was one of the products of decomposition of the bile of the pig.

Moreover, the author has already pointed out the relations which hyocholic acid exhibits to one of the constituents of the bile of the ox—cholic acid. He had found that, on the escape of the elements of water, an acid is formed from cholic acid which closely resembled hyocholic acid, the formula of which differs by C^2H^2 from that of the former, and which may be regarded as an acid homologous to it. Mulder has denominated this acid cholonic acid (*Scheik. Onderzoek.* 5 Deel, p. 26). Strecker has retained this name, and in his formulæ of these acids has expressed the above statement by the following equation: $C^{54}H^{43}NO^{10}$ hyocholic acid $= C^2H^2 + C^{52}H^{41}NO^{10}$ cholonic acid.

The author long since pointed out the consequent probability, that hyocholic acid is also a conjugate glycocoll compound, from its divisibility into glycocoll and a non-nitrogenous substance to which he directed attention. The author also proved some time since, in conjunction with Gundelach, that the precipitate thrown down by æther from the alcoholic solution of the bile of the pig contained 0·47 per cent. of sulphur; Bensch found 0·3 per cent. in it. In an investigation made by Van Heijningen and Scharlée (*Scheik. Onderz.* 5 Deel, p. 105–132), the total amount of sulphur in the bile of the pig was determined. The bile was evaporated, and the residue dried at 248° F. It contained inappreciable traces of sulphuric acid. On combustion with hydrate of soda and nitre, the total amount of sulphur contained in it was determined and the following results obtained:—

	I.	II.	III.	IV.	V.
Sulphur	1·67 1·36	1·37 1·47	0·81 0·86	1·01 0·91	1·93 1·88

These determinations of the sulphur differ from those of Bensch, Gundelach and Strecker; whilst Van Heijningen and Scharlée, in conformity with the statements of the above chemists, obtained 0·40 per cent. of sulphur from the organic substance in the lead precipi-

tate from the bile of the pig. These quantities of sulphur are especially favourable to the view, that a conjugate taurine compound is contained in the bile of the pig; its quantity, however, must be very small, since the total amount of sulphur does not exceed 0·5 per cent. of the bile.

Strecker has since examined the products of decomposition of this bile; and, as the experiments of Van Heijningen and Scharlée have yielded a different formula, because they analysed hyocholic acid, which was not sufficiently free from the sulphuretted hyocholeic acid, he has repeated the analysis of the latter acid. The hyocholic acid may be separated from the hyocholeic acid, as also from the colouring matter, although with a small loss, by precipitating the soda-salt from the aqueous solution by sulphate of soda. The soda-salt thus separated is dissolved in alcohol, treated with animal charcoal, precipitated by æther, and the acid then separated from it by muriatic acid. The acid dried at 266° F. yielded—

Carbon.....	70·16	54	70·28
Hydrogen.....	9·51	43	9·33
Nitrogen	..	1	3·04
Oxygen.....	..	10	15·35
			100·00

This result agrees perfectly with the earlier ones of Strecker and Gundelach. The products of decomposition of the bile of the pig, just as is the case with this bile and that of the ox, stand in intimate relation with the products of decomposition of the bile of the ox.

Hyocholic Acid and Muriatic Acid.—When hyocholic acid is boiled for a long time with concentrated muriatic acid it melts, and on cooling again solidifies to a resinous mass. If, after this treatment, the aqueous liquid be evaporated to dryness, a small crystalline residue is left. After ebullition for several days, the muriatic acid being frequently replaced, the resinous mass becomes constantly less fluid, and at last remains in a state of almost complete solidity in the boiling liquid. On cooling, the mass may be readily powdered; boiling water then extracts all those constituents which are soluble in it. The resinous mass which remains insoluble in the water differs in its reactions, and exhibits a varying composition according to the duration of the ebullition. At first it is readily soluble in alcohol and ammonia, whilst it is but little soluble in æther; afterwards its solubility in alcohol diminishes; it swells up in ammonia into a mucoid, turbid liquid, and at last it is not at all soluble in cold alcohol, and but little so in boiling alcohol, whilst it is pretty freely dissolved by æther. The amount of carbon contained in it varied at different periods from 73·0 to 74·5 per cent.

The final product is a substance which much resembles the dyslysine of the bile of the ox. On solution in æther and precipitation by the addition of alcohol, it is obtained in a slightly coloured state. It is perfectly insoluble in ammonia, soluble in an alcoholic solution of potash; and after fusion with the hydrate of potash, no ammonia

being evolved, it is soluble in water. After having been dried at 248° F., it yielded on analysis,—

Carbon	77·61	50 =	300	77·72
Hydrogen	9·97	38 =	38	9·84
Oxygen	12·42	6 =	48	12·44
	100·00		386	100·00

The relation of this substance to the dyslysine of the bile of the ox is the same as that of hyocholic acid to cholonic acid: $C^{48} H^{36} O^6 + C^2 H^2 = C^{50} H^{38} O^6$. Its formation from hyocholic acid may be thus represented: $C^{54} H^{43} NO^{10}$ hyocholic acid—$C^{50} H^{38} O^6 = C^4 H^5 NO^4$ (glycocoll).

Its decomposition by muriatic acid, however, is not so simple; and non-nitrogenous intermediate products are first formed, which contain one or more equivalents of water.

The glycocoll remains after this decomposition in combination with muriatic acid dissolved in the acid liquid, and on the evaporation of the latter is obtained in the form of a brown crystalline mass. This is dissolved in water, treated whilst boiling hot with hydrated oxide of lead, and the lead removed from the filtered liquid by sulphuretted hydrogen; prismatic crystals of glycocoll are then obtained on evaporation. The crystals of glycocoll thus obtained, after having been dried in the air, do not lose weight at 212° F., and yielded on analysis 31·8 carbon and 6·7 hydrogen per cent.; moreover, on boiling them with peroxide of copper, a blue solution was obtained; this on the addition of alcohol deposited blue needles, which possessed the properties of the compound of glycocoll and peroxide of copper. This compound was dried at 212° F., during which process it lost water; and when subsequently incinerated, left 37·2 per cent. of peroxide of copper. The formula of the compound of glycocoll and peroxide of copper, dried at 212° F., is, according to Horsford, $C^4 H^4 NO^3$, CuO, and requires 37·6 per cent. of peroxide of copper.

Hyocholic Acid and Alkalies.—Dilute solution of potash dissolves hyocholic acid without change; and when the ley has become concentrated by evaporation, the hyocholate of potash again separates upon the surface of the solution. If the ebullition be continued for twenty-four hours, the evaporated water being replaced, the hyocholic acid becomes converted into a new acid, hyocholalic acid, which must be precipitated by muriatic acid and dissolved in æther. It is obtained in a crystalline state from this solution.

Hyocholalic Acid, $C^{50} H^{40} O^8$, dissolves in large quantity in alcohol, less readily in æther. In water it is but very slightly soluble. The alcoholic solution leaves it on evaporation in the form of an amorphous mass; on the addition of water, it is sometimes obtained from a dilute alcoholic solution in small crystals, which appear under the microscope to be hexagonal plates. The same crystals are very easily obtained when a little æther is present. In general this acid exhibits but little tendency to crystallize, and is much more easily obtained in the amorphous than in the crystalline modification, in which respect it differs essentially from cholalic

acid. In dilute solutions of the hydrate or carbonate of potash, the potash salt is again separated. The solution of hyocholalic acid in ammonia yields flaky precipitates with salts of lime and baryta, as also with almost all solutions of the heavy metallic oxides. The analysis of the hyocholalic acid, dried at 248° F., yielded—

Carbon.....	74·5	..	74·1	74·2	50	= 300	74·25
Hydrogen ..	10·3	9·9	10·0	10·0	40	= 40	9·90
Oxygen	..	..	..	..	8	= 64	15·85
						404	100·00

Hyocholalate of Baryta, BaO, $C^{50} H^{40} O^8$, which is obtained by dissolving the acid in ammonia, precipitation with the chloride of barium, washing with water, solution in alcohol and evaporation, is difficultly soluble in water; the aqueous solution has a strongly bitter taste; it is precipitated both by acids and by acetate of lead.

The analysis of the salt, dried at 320° F., yielded the following results:—

Carbon.....	62·3	62·2	62·3	50	= 300·0	62·43
Hydrogen ..	8·4	8·4	8·4	40	= 40·0	8·32
Oxygen	..	..	..	8	= 64·0	13·33
Baryta.....	15·9	..	..	1	= 76·5	15·92
					480·5	100·00

It appears from the results of this analysis, that the hyocholalic acid has combined with the baryta without giving up an equivalent amount of water. The same relation has already been shown to occur in the case of hyocholic acid. To decide more positively upon this circumstance, the author again dried the baryta salt, which had been already dried at 320° F., at 356° F.: it then lost 1·8 per cent. A second quantity, which had been dried at 266° F., lost at 392° F. 1·4 per cent. of water. If one equiv. of hyocholalate of baryta, $C^{50} H^{40} O^8$, BaO, lost one equiv. of water, the decrease in weight should amount to 1·8 per cent. The barytic salt, dried at 392° F., yielded on analysis,—

Carbon.....	63·1	50	= 300·0	63·6
Hydrogen	8·5	39	= 39·0	8·3
Oxygen	..	7	= 56·0	11·9
BaO.....	15·9	1	= 76·5	16·2
			471·5	100·0

Hence the formula of the dry hyocholate of baryta appears to be BaO, $C^{50} H^{39} O^7$.

The resolution of the hyocholic acid into glycocoll and hyocholalic acid may therefore be expressed by the following equation:—

$C^{54} H^{43} NO^{10}$ (hyocholic acid) $+ 2HO = C^{50} H^{40} O^8$ (hyocholalic acid) $+ C^4 H^5 NO^4$ (glycocoll).

Thus on the decomposition of hyocholic acid, as in that of cholalic and hippuric acids, two equivalents of water are assimilated, a coincidence which is favourable to the correctness of the formulæ.

The very remarkable circumstance that the bile of the pig contains, in hyocholic acid, an acid which differs from the non-sulphuretted acid of the bile of other animals, is rendered still more evident by the detection of the base which is about to be described, and which has not hitherto been found in other kinds of bile. Thus, when the fresh bile of the pig is precipitated with dilute muriatic acid, a very small quantity only of organic substance remains in solution; and a deep yellow mass, which is at first soft and mucoid, and subsequently becomes more pulverulent, separates. After having been washed with water and boiled with concentrated muriatic acid, this acquired a deep green colour, and finally became hard and pulverulent; it was finely pulverized, and repeatedly boiled with water. The muriatic acid which was poured off, and the other aqueous fluids obtained by the ebullition, were evaporated together, when a dark-coloured residue was left, which consisted principally of muriate of glycocoll. It was dissolved in water, boiled with hydrated oxide of lead as long as ammonia continued to escape, and the lead precipitated from the filtered solution by sulphuretted hydrogen, when an almost colourless liquid was obtained. On the addition of sulphuric acid and evaporation in the water-bath, the residue was dissolved in absolute alcohol, when sulphate of glycocoll and traces of sulphate of soda remained undissolved. On the addition of chloride of platinum and muriatic acid, a pale yellow flocculent precipitate was obtained from this solution, which dissolved readily in water, and on evaporation crystallized in needles. It was also precipitated from the aqueous solution by alcohol. The substance combined with the chloride of platinum is a powerful organic base, which renders reddened litmus-paper blue; all its salts are soluble in water, and most of them also in alcohol. By treatment with sulphuretted hydrogen, the base could be separated from the platinum; by evaporation with sulphuric acid, a sulphate was obtained, which was again dissolved in absolute alcohol and decomposed by carbonate of baryta. On strongly concentrating the solution, indistinct crystals were obtained, which burned completely on platinum-foil, had an alkaline reaction, and on the addition of muriatic acid, evolved carbonic acid. After combustion with potash and nitre, ammonia being evolved, a considerable amount of sulphuric acid could be detected in the residue. This base has not yet been obtained in sufficient quantity to allow of its more minute examination; but, from the sulphur it contains, and its property of combining with carbonic acid, it is well-worthy of attention.

The whole of Strecker's investigations upon the bile of various animals, including the preceding details, show that the bile of most animals essentially contains the same constituents, and that the difference between them depends principally upon the proportions of the substance containing sulphur, and that free from it. The examination of the bile of the dog fed with flesh, as also of that consuming a vegetable diet, showed that the difference of the food does not exert any perceptible influence upon the composition of the bile

of the same animal. That the difference in the relative admixtures of the two principal constituents of the bile in different genera of animals cannot be referred to a difference in the food, is shown by the comparison of the bile of the ox and that of the sheep. The proportion of the two principal constituents of the bile of the latter approximates much more to that which is found in the bile of the serpent and salt-water fish, than that of the bile of the ox.

The author then dwells upon the difference exhibited by the bile of the pig, since, with the peculiarity of its products, it forms an isolated example. The author has not further traced the remaining constituents of the various kinds of bile; since that portion of them which is soluble in alcohol and insoluble in æther alone constitutes more than 75 per cent., they are present in small quantity only. In all the kinds of bile, biliary mucus, cholesterine and fat were met with.—*Ann. de Chem. und Pharm.*, vol. lxx. p. 149–198.

Chemical Examination of Coprolitic Remains from different parts of England. By Thornton J. Herapath, *Esq.*

To the Editor of the Chemical Gazette.

Mansion House, Old Park,
Bristol, Nov. 3, 1849.

My dear Sir,

In a recent Number of the Chemical Gazette* there was inserted a short paper of mine on the analysis of a peculiar phosphatic earth from Sussex, which was stated to have been found in large quantity in many districts of that and some other counties, particularly in the lower beds of the cretaceous system, and had been lately introduced to a considerable extent as a substitute for bone-earth in the preparation of superphosphate of lime for agricultural purposes. Since the publication of that notice, I have had occasion to examine professionally several other coprolitic remains from different parts of England. These bodies, I need hardly remind you, are supposed by geologists to be the fossilized excrements of the ichthyo- and plesiosauri; and are now, in consequence of the extraordinary fertilizing powers they have been discovered to possess, most extensively used in commerce for similar purposes to the above. As the results of my analyses may contribute in some measure towards rendering our knowledge of the composition of these coprolites more complete, and their value as a manure more generally known, I have no doubt but that you will do me the favour to make my scientific brethren acquainted with them, through the medium of your pages, in the shape of an appendix to my former paper.

I. The following are the analyses of two coprolites from the coast of Suffolk. These were of an oval form, weighing between six and seven hundred grains each, and their external surfaces were much water-worn and highly polished. Their colour was brownish-ferru-

* No. 152, vol. vii. p. 70.

ginous; they were easily fractured, and, when triturated in an agate mortar, yielded a yellowish-red powder. The specific gravity, at 60° F., was 2·815 or 2·850.

Composition per cent.—

	I.			II.		
Water with a little organic matter	4·000			3·560		
Salts soluble in water (chloride of sodium and sulphate of soda)	traces			traces		
Carbonate of lime	10·280			8·959		
Carbonate of magnesia	a trace			a trace		
Sulphate of lime	distinct traces			0·611		
Phosphate of lime ($3CaO, PO^5$)	70·920 =	PO^5	32·765	69·099 =	PO^5	31·924
Phosphate of magnesia	traces only			traces		
Perphosphate of iron ($2Fe^2O^3, 3PO^5$)	6·850 =	PO^5	3·244	8·616 =	PO^5	4·081
Phosphate of alumina ($2Al^2O^3, 3PO^5$)	1·550 =	PO^5	0·870	2·026 =	PO^5	1·158
Oxide of manganese	traces			0·016		
Fluoride of calcium	0·608			0·804		
Silicic acid, coloured red by a little undecomposed silicate of iron	5·792			6·309		
	100·000 =	PO^5	36·889	100·000 =	PO^5	37·16

50 grains of the first specimen, in fine powder, when burnt with potash-lime, furnished 0·20 gr. of platino-chloride of ammonium, which is equivalent to 0·0254 per cent. of nitrogen.

It is said that the coprolites which Mr. Lawes employs in the manufacture of his well-known "Coprolite Manure," are obtained from the Suffolk coast, and are similar in character to the above*.

II. This one was brought from the same part of the coast as the preceding; but differed from them in its irregularity of form, and in exhibiting imperfect evidences of a bony structure. The specific gravity, it was found impossible to determine, on account of the numerous air-cavities it contained.

Analysis showed it to possess the subjacent per-centage composition:—

* In an excellent paper "On the Phosphoric Strata of the Chalk Formations," published in the first number of the Journal of the Royal Agricultural Society of England for last year, Mr. Way observes, that he has found the coprolites from this district to contain from 52 to 54 per cent. of bone-earth phosphate, and that Dr. Gilbert had informed him, that in several analyses which he had made of samples taken from several tons of the ground coprolites, he had found the proportion of phosphate of lime to vary between 55 and 57 per cent. Mr. Nesbit (Quart. Journ. of Chem. Soc., Part III. p. 235) found from 22·30 to 28·74 per cent. of phosphoric acid, which is equivalent to from 48·31 to 59·07 of tribasic phosphate, in those from the tertiary deposits of this county.

Water driven off at from 300° to 350° F.	2·600	
Water and organic matters expelled at a red heat	9·000	
Chloride of sodium, &c.	evident traces	
Carbonate of lime	39·500	
Carbonate of magnesia	0·520	
Sulphate of lime	distinct traces	
Phosphate of lime (tribasic)	15·860 = PO^5	5·287
Phosphate of magnesia	traces	
Perphosphate of iron	9·200 = PO^5	4·358
Phosphate of alumina	4·708 = PO^5	2·764
Peroxide of iron	none	
Alumina	6·212	
Fluoride of calcium	1·698	
Silicic acid	10·601	
	99·899 = PO^5	12·409

The proportion of nitrogen in this specimen was not estimated.

III. This coprolite was discovered in the lias strata of Lyme Regis, and was kindly presented to me by my esteemed friend, Edward Barker, Esq. of Budleigh Salterton.

It was rather large, being above nine ounces in weight, was of a grayish colour, and, when broken, exhibited some traces of a crystalline structure. It was considerably softer than either of the preceding, and furnished a grayish-white powder. Many scales of different extinct fishes, and other organic remains, were to be perceived on the external surface; the greater proportion of them appeared to belong to a species of fish which is known to ichthyologists by the name of *Pholidophorus limbatus*. Its specific gravity was about 2·644 or 2·700, and the composition per cent. was as follows:—

	I.	II.	Mean.	
Water driven off at from 300° to 350° F.	2·560	2·668	2·6140	
Water and organic matters expelled at a red heat	3·680	3·456	3·5680	
Chloride of sodium, with some sulphate of soda	traces	traces	traces	
Carbonate of lime	23·640	23·708	23·6740	
Carbonate of magnesia	none	none	none	
Sulphate of lime	1·740	1·801	1·7705	
Phosphate of lime (tribasic)	60·726	60·813	60·7695 = PO^5	28·047
Phosphate of magnesia	a little	a little	a little	
Perphosphate of iron	3·980	4·135	4·0575 = PO^5	1·922
Phosphate of alumina	a little	a little	a little	
Peroxide of iron	2·094	1·894	1·9940	
Alumina	none	none	none	
Silicic acid, with fluoride of calcium and loss	1·580	1·525	1·5525	
	100·000	100·000	100·0000 = PO^5	29·969*

The proportion of nitrogen in this specimen was rather large, being 0·0826 per cent.

Yours very truly,

THORNTON J. HERAPATH.

* In the first of these analyses, the phosphoric acid was estimated by M. Schulze's method, as perphosphate of iron; in the second, as phosphate of lead.

On the Non-volatile Acids of the Root of Valeriana officinalis.
By E. Czyrnianski.

Several years ago Runge stated that an acid occurred in the roots of valerian and in those of Scabious which gave, with bases, white salts that became green by exposure to the air. He called it viridous (*grünige*) acid, and the green product of oxidation viridic (*grün*) acid. The properties of this acid, described by Runge, led me to suppose that it might perhaps prove identical with catechutannic acid, $C^{14} H^7 O^7$, or with caffeotannic acid, $C^{14} H^8 O^7$.

Fresh valerian roots were exhausted with hot anhydrous alcohol, and the filtered liquid precipitated with an alcoholic solution of neutral acetate of lead, when a dirty white precipitate fell. This precipitate was collected on a filter, washed with boiling alcohol, suspended in water, and decomposed with sulphuretted hydrogen, when it furnished a liquid which, separated by filtration from sulphuret of lead, and freed from excess of sulphuretted hygrogen, gave with a solution of acetate of lead, a white precipitate with a somewhat yellowish tint, which became green by exposure to the air for a couple of hours. The composition of this lead salt, dried *in vacuo*, was—

Carbon	17·41	17·49
Hydrogen	1·79	1·93
Oxygen	13·63	13·41
Oxide of lead	67·17	67·17

These numbers correspond most closely to the formula $C^{14} H^9 O^8$, which is the same as one equiv. caffeotannic acid + one equiv. water.

The free acid experiences rapid decomposition in the air, especially at a high temperature. It very quickly reduces salts of silver. It is distinguished from caffeotannic acid by its behaviour towards persalts of iron and ammonia; it is not rendered green by the former, and acquires by standing in an atmosphere of ammonia a brown, and not a green colour. It furnishes a white compound with baryta, which turns brown in the air; sulphuric acid colours it red and decomposes it.

The liquid filtered from the first precipitate furnished a copious precipitate on being mixed with some ammonia; it was collected and decomposed with sulphuretted hydrogen; the liquid filtered from the sulphuret of lead gave, with tribasic acetate of lead, a white precipitate, which furnished, on analysis, the following results:—

Carbon	15·15	15·16
Hydrogen.....	1·75	1·64
Oxygen.....	14·25	14·34
Oxide of lead ..	68·86	68·86

which corresponds to the formula $C^{12} H^8 O^9$.

The acid of this salt has a slightly acid taste, and appears to crystallize on careful evaporation in a current of hydrogen. It also reduces the salts of silver, but does not furnish an insoluble baryta salt.—Liebig's *Annalen*, July.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On a Simple and Certain Test of the Quality of Indigo. *By* H. Reinsch.

Reinsch tried various modes of determining the goodness of indigo —such as the external appearance; the intensity of colour imparted to yarn by the cold vat (made of indigo, lime, sulphate of iron, and water); the quantity of indigo-blue obtained by sublimation; the quantity of indigo-blue deposited from the cold vat; and the specific weight. Not one of these methods, however, gave results to be relied on.

"At last," he says, "I resorted to fuming sulphuric acid, and obtained the most satisfactory results. It is necessary, however, that the indigo should be pounded very fine, and the acid should be as concentrated as possible. I must also observe, that the solution of the Java indigo, and of that indigo which I prepared in a chemical way, by treating it with acid, caustic potash, spirit of wine and water, did not possess that pure blue colour like that of the Bengal sort, although I repeated the experiments several times, and could not, therefore, determine anything with regard to the purified indigo. A dyer of great experience informed me, that for solution in sulphuric acid he prefers Bengal to the Java sort, as the latter is burnt by the acid, which is always the case when the indigo does not dissolve with a pure blue colour, but assumes a crimson hue on the sulphuric solution being poured in water.

"The mode in which I proceed is as follows:—$\frac{1}{10}$th gramme of each sample of indigo is well pounded, mixed with four or five drops of fuming sulphuric acid, and rubbed with it until the whole forms a brown uniform mass. To this 1 grm. of sulphuric acid is added, and triturated till it produces a clear green solution, whereupon another gramme of fuming sulphuric acid is added; lastly, this solution is gradually mixed with 10 grms. of water. Two glass cylinders of equal length and width are now divided each into twenty equal parts, and 1 grm. of the sulphuric solution (which is best measured by a glass tube closed at one end) poured into one and mixed with water, till the solution is of a light-blue colour and transparent; if 1 grm. of the solution does not produce sufficient coloration, a small quantity more of it is added, till the cylinder is filled with the light-blue solution. I generally commence with the apparently best indigo. After this the second cylinder is filled in the same way with an equal quantity of sulphuric solution of the same indigo sample and water, in order to see whether the two solutions are equal in colour. If this be the case one of the cylinders is emptied, and an equal quantity of sulphuric solution of an inferior sample poured into it and gradually diluted with water, till the solutions in both cylinders are perfectly alike in colour. Care is to be taken that the coloration be not too intense nor too light, it being in either case difficult to obtain both solutions of the same hue.

For discovering this equality the eye will also be much assisted if the relative position of the cylinders is changed from the right to the left, or by placing them alternately before or behind one another. As soon as the colour of both is thus found to be equal, the quantity of water is examined which has been poured into the second cylinder. Supposing now that 1 grm. of sulphuric solution has been employed in either of the cylinders, but the quantity of water which produced the equal colour was in the first or standard cylinder 20 parts, and in the second only 15 parts, then the sample of which the latter solution was made will contain $\frac{5}{20}$ths, or one quarter less of colouring matter. In order to guard myself against all deception, I had several such samples prepared by one of my pupils, and upon subjecting them to this test I always discovered the correct quantity.

"This method is so easy and convenient that everybody can avail himself of it. All that is required is to keep ready a certain quantity of indigo-solution of a known quality as standard solution, and then to prepare a sulphuric solution of the indigo to be tested. I have before observed that the purified indigo did not give the desired results, and I used, therefore, Bengal, first quality, which excelled all others in colouring capacity, and contained at least 50 per cent. pure colouring matter.

"The results were: Bengal as standard =20.

	First Exp.	Second Exp.
Bengal, first quality, from another source ..	20	$20\frac{1}{2}$
Bengal, II.	19	19
Bengal, III.	7	8
Java, I.	19	$19\frac{1}{2}$
Java, I., from another source	19	$18\frac{1}{2}$
Java, middling fine	18	18

"The third quality of Bengal presented a very dirty blue solution, yet it has been declared by a dyer of great practice as perfectly adapted for the warm colour; but as the blue from the warm vat is rather a dirty brownish-blue, it is certainly possible that the dyer can make use of it for the warm colour; it is, however, quite unfit for the cold vat, and for Saxon blue (sulphuric solution of indigo). For medical purposes it ought never to be used, for it is probably nothing but the lowest sediment of the indigo.

"The above-described method may even be made more accurate if longer glass cylinders are used, so that the per-centage quantities may be indicated. The glasses must then be divided in 100 parts. The larger the degrees are, the more accurate will the results be.

"I have yet to add some observations with regard to an adulteration practised on the indigo, and which is of importance to the druggist. Each large indigo-chest contains a quantity of dust, which is said to amount sometimes to 8 or 10 pounds. This dust is an artificial product, composed of starch or white lead and powdered indigo, and is put in the chest in order to increase its weight.

"If we now consider the present price of indigo, we find the finest Bengal to cost 4 florins 30 kreutzers per lb., the finest Java

indigo being the same price; still Bengal is always to be preferred. The middle sort of Bengal costs 3 florins; the low, No. III., 2 florins 20 kreutzers; but what a difference in their colouring properties! Bengal No. II. is nearly, if not equally, as good as No. I., and its price is only two-thirds of that of the latter. Bengal, III., on the contrary, is sold at half the price of No. I., and is worth, as dyeing material, but one-third. These points are certainly deserving the consideration of the dyer in pecuniary respects, and they will be of equal importance for the physician, if the medicinal principle in indigo should be discovered as distinctly as was that in the sponge and goitre-stone [kropfstein, *Cellepora spongites*] by the discovery of iodine."—*Jahrbuch fur Praktische Pharmacie*, and *Pharmaceutical Journal*.

PATENTS.

Patent granted to Robert Oxland and John Oxland *for Improvements in the Manufacture of Sugar.*

These improvements in the manufacture of sugar consist in the employment of the acetate of alumina for defecating cane- and beet-root juice, and of both defecating and removing the colour from the solutions of raw sugar, produced in the operations of sugar refining.

The process for sugar refining is conducted in the following manner:—The raw sugar may be blown up in the usual manner, but it is preferred to dissolve the sugar in water, with the aid of heat from steam, passing through a flat coil of pipe, into an outer jacket surrounding the pan, and then carbonate of lime, in fine powder, should be mixed with the syrup, until all acidity be neutralized, and the solution should be made to boil at a temperature of 220° Fahrenheit. The syrup should then be run into the ordinary filter-bags, and when running bright from them, it should be turned into another but more shallow blow-up pan, fitted in the same manner as before described. Acetate of alumina is now to be mixed with the syrup, and the whole boiled together at a temperature of 220°, until the greater portion of the acetic acid has been evolved, which may be ascertained by testing the steam passing off from the syrup with blue litmus paper. A steam-tight cover and pipe, fitted to a condensing apparatus, may be employed to save the acetic acid evolved, which may be used for the preparation of further quantities of acetate of alumina. When nearly the whole of the acetic acid has been evolved, small quantities of a solution of tannin in water are stirred in until no further precipitate is produced thereby. The process is completed by the addition of carbonate of lime, in fine powder, in sufficient quantity to neutralize all acidity. The syrup is then passed through bag-filters, and as soon as it runs bright, it is turned into the reservoir from which the vacuum-pan is supplied. It has been found that one filtration through the bags is sufficient, provided a larger quantity of acetate of alumina be employed, and a fine copper sieve be interposed between the liquor running down from the blow-up pan and the head of the bag-filters.

The boiling in the vacuum-pan is conducted in the usual manner, as are also the whole of the subsequent operations. In the prepara-

tion of fine liquor, to be employed subsequently to what is termed the claying operation, it has been found desirable to use a small quantity of acetate of alumina, heating the syrup to which it has been added to 212° Fahr. for a few minutes, then adding sufficient of the solution of tannin, to precipitate the last traces of alumina, and of carbonate of lime, to neutralize acidity; and finally, passing through filter-bags. Cane- and beet-root juice are treated with the acetate of alumina and solution of tannin for defecation, either before the neutralization by lime and concentration by heat, or subsequently, when the juice has been concentrated to from 20° to 28° Baumé.

The acetate of alumina is prepared in the following manner:—Sulphate of alumina is dissolved in cold water, and a clear solution of soda-ash, also made in cold water, added to it, until an alkaline reaction is produced on reddened litmus paper. The liquor is allowed to stand until the alumina is precipitated, the clear liquor then drawn off, and the precipitate washed with a fresh quantity of water, which is again removed, and the washing repeated until the hydrometer no longer indicates the presence of any soluble matter.

The precipitate is taken with as little water as may be, and acetic acid added in successive quantities, until the whole or nearly all of the alumina is dissolved, avoiding an excess of acid. The acetate of alumina acts best when recently prepared.

The solution of tannin is prepared by digesting one pound of crushed valonia in two gallons of hot water, using the clear liquor; but it may be prepared by other means. As different sugars differ in their qualities, no exact rule can be given as to the quantity of acetate of alumina to be used; but the operator will readily ascertain the quantity required in each case, by taking a sample of the juice or sugar, and testing it with a measured quantity of acetate of alumina. The patentees have found that the best effect is produced on a fair sample of Jamaica sugar, by employing at the rate of four pounds of alumina, dissolved in acetic water, to one ton of sugar.—April 26, 1849.

Patent granted to Achille Chaudois *for Improvements in extracting and preparing the colouring Matter from Orchil.*

In the ordinary mode of obtaining colouring matter from dye lichens or orchil, as much water is combined with the lichens or orchil as will bring the same to a pasty state, and then alkalies, such as liquid ammonia, are added (in some cases potash or urine and lime are used for the same purpose); but the colouring matter obtained in this way is not so pure as that obtained by the process which forms the subject of this invention, because the colouring extract is mixed with the "substantive" parts of the lichens or orchil. The patentee subjects the lichens or orchil to repeated washings in water until he has extracted the whole of the colouring matter therefrom; and then he treats the water in the same manner as the paste above-mentioned has been hitherto treated. The lichens or orchil may be washed in hot water only, or in water containing alkaline matters.—Sealed Feb. 14, 1849.

THE CHEMICAL GAZETTE.

No. CLXXI.—December 1, 1849.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Researches on Caffeine. *By* F. Rochleder.

Some time ago I published a short notice on the decomposition which caffeine experiences by oxidizing agents. I then stated that in this process the caffeine furnishes a basic and a weak acid substance, which latter exhibits all the reactions characteristic on the one hand of alloxan, and on the other of alloxantine. I have examined these changes more closely, and have ascertained the composition of these products. In the following pages I shall describe their preparation and the results of their analysis, and leave to another occasion the behaviour of these products towards other bodies, by means of which I hope to establish their constitution. This investigation will show the part which caffeine is capable of acting in the animal body.

When a rapid current of chlorine is passed through a thick paste of crystals of caffeine, the liquid becomes heated, without however attaining to ebullition. It is readily seen whether the action is terminated, by discontinuing the current of chlorine and letting the warm liquid cool. When, on renewing the transmission of the chlorine through the liquid, it no longer becomes heated, it is a sign that the decomposition is perfect. If from time to time a drop of the liquid is mixed with a drop of caustic potash, a white precipitate results so long as undecomposed caffeine is present, which appears under the microscope as a tissue of white shining needles. The liquid obtained by treating caffeine with chlorine contains four different substances besides chlorine in solution, muriatic acid, the muriate of a base, a weak acid, and lastly, an extremely volatile product, whose composition and properties I endeavoured in vain to ascertain, as it was impossible to procure even a small quantity pure.

When this liquid is heated in a water-bath, numerous bubbles of gas escape, chlorine, muriatic acid, and the above-mentioned volatile body are expelled, which makes its presence known by its disagreeable odour. It irritates the eyes, producing a flow of tears, and the smallest quantity causes an insupportable headache in the frontal part. It was found impossible to isolate the small quantity of this substance, from the large quantity of muriatic acid and chlorine accompanying it.

On evaporating the liquid in an open dish on the water-bath, a large quantity of muriatic acid is driven off; this proceeds from the decomposition of the water, the oxygen of which oxidizes the caf-

feine, from which no hydrogen is taken to be replaced by chlorine. When the liquid is concentrated to within two-thirds of its bulk, crystals begin to separate, which gradually increase in quantity. When they no longer increase, the liquid is allowed to cool and separated from the crystals. These are then washed with cold water, in which they are nearly insoluble, and exhausted with boiling absolute alcohol. After this treatment they are nearly pure; they can however be purified by solution in boiling water, from which they separate when the liquid is agitated, but when left quiet, crystals of larger dimensions are formed in the course of several hours. They are perfectly transparent, colourless, almost insoluble in absolute alcohol, very sparingly soluble in cold, and only to a slight extent in hot water. They contain no water which can be expelled at 212°, dried at which temperature they have the same composition as when dried *in vacuo*. They redden very faintly litmus paper, and become coloured of a rose-red by the ammonia of the blue litmus paper. This substance forms combinations with baryta, potash and soda, which have a dark violet blue colour. When a solution of these bases is added to the crystals of this acid, they are instantly coloured violet, whilst the liquid remains colourless. With an excess of the bases this colour is transitory, whilst with an excess of the acid it is pretty constant. I have called this substance *amalic acid*, to indicate on the one hand its weak acid nature, and on the other the slight stability with which its elements are combined.

Ammoniacal vapours redden the acid, which at first passes slowly but gradually into a dark violet colour. The substance thus formed dissolves in water with the colour of murexide; no crystals of murexide are obtained from this solution; moreover the liquid is instantly decolorized by the addition of potash without the colour previously passing into blue. These most splendidly coloured liquids are most easily obtained in the following manner. Either some concentrated solution of chloride of ammonium is heated with it to boiling and a drop of solution of ammonia added to the liquid, or the crystals are placed upon a watch-glass, and some ammonia in a second, and both covered with a bell-glass. In a short time the crystals become dark violet and then dissolve in water with the colour of murexide*. With protosalts of iron and ammonia a saturated indigo-blue solution is formed. The substance melts when heated, turns yellow, reddish yellow to brown, and is volatilized, leaving scarcely perceptible traces of carbonaceous residue; at the same time ammonia is evolved, and an oily and a crystalline substance are formed. The solution of this substance produces the same disagreeable smell and red stain upon the skin as a solution of alloxan. Amalic acid reduces salts of silver, with separation of black flakes of metallic silver, like alloxantine. When boiled with nitrate of silver and nitric acid, the acid is decomposed; not a trace of chloride of silver is formed: amalic acid contains no chlorine. When heated with nitric acid, it is converted into a new crystalline substance,

* I have procured this substance pure in the crystalline state, and shall describe its properties and composition on a future occasion.

with evolution of red vapours. The acid burns with difficulty; to obtain perfect combustions, it was mixed with chromate lead and a layer of oxide of copper, and then copper turnings which had been reduced with hydrogen were inserted in the combustion-tube; the nitrogen was determined according to the qualitative method, (when the proportion of carbon to nitrogen was found to be as 6 : 1), and also according to the method of Will and Varrentrapp. The following are the results of the analysis :—

Carbon	41·83	42·04	42·04	..	12 =	900·0	42·10
Hydrogen ..	4·35	4·17	4·27	4·18	7	87·5	4·09
Nitrogen	..	16·33	16·30	..	2	350·0	16·37
Oxygen	..	37·16	37·39	..	8	800·0	37·44

I now return to the liquid from which the crystals of amalic acid had separated; this was evaporated in the water-bath to expel the greater portion of the free muriatic acid; in this operation it acquires a faint yellowish colour with a slight reddish tint. If the liquid, when it has been evaporated to within a fourth of the original bulk, is allowed to cool, it congeals to a mass of crystals which enclose a thick tenacious mother-liquor. This mass is brought upon a double layer of fine linen, and the crystals separated from the ley by careful pressure; they are then purified by solution in hot water or alcohol, when they separate in the form of a laminar, colourless, crystalline mass, fatty to the touch, the solution of which furnishes with chloride of platinum a copious yellow precipitate, and with nitrate of silver a copious precipitate of chloride of silver. These crystals are the muriate of a base, the composition of which I have ascertained by the analysis of its platinum double salt.

I adopted several different methods for the separation of the platinum salt in order to assure myself of its constant composition. The mother-liquor from the amalic acid was mixed with a solution of chloride of platinum, the precipitate collected on a filter, dissolved in a sufficient quantity of boiling water, and the concentrated solution set aside to cool. A beautiful yellow salt in granular crystals and of considerable lustre falls, which acquire a cinnabar-red colour when heated, but again become yellow on cooling. The crystals dried *in vacuo* were employed for analysis I. The mother-liquor from these crystals was mixed with absolute alcohol, when a quantity of iridescent, pale yellow hexagonal plates were precipitated, which were collected on a filter, washed with alcohol, dried *in vacuo*, and used for analysis II. For analysis III., the large laminar crystalline salt of the base was dissolved in alcohol, and precipitated with a spirituous solution of chloride of platinum; the pale yellow precipitate exhibited not a trace of crystallization. The mother-liquor from the crystals used for II. was concentrated, and the yellow deposit recrystallized from hot water. The crystals obtained served for analysis IV. The solution of caffeine treated with chlorine was directly precipitated with chloride of platinum, the precipitate collected, washed with alcohol, and used for determination V. The smaller amount of platinum found in V. shows that the precipitate was not pure; I have

inserted it, as it proves that not a trace of ammonia is formed in the oxidation of the caffeine. Were such the case, the impure platinum salt should have given a greater amount of platinum. The following is the composition :—

	I.	II.		III.	IV.	V.			
C.	4·87	4·86	..	..	..	..	2 =	150·0	5·09
H.	2·49	2·49	2·42	..	..	..	5	62·5	2·12
N.	..	..	..	..	..	..	1	175·0	5·94
Cl.	..	..	..	..	..	..	3	1329·8	45·08
Pl.	41·42	41·43	..	41·61	41·42	41·06	1	1232·1	41·77

The formula of the platinum double salt is consequently $C^2 H^4 N$, $Cl H + Pt Cl^2$; and the composition of the base contained in it, which I have named formyline, is expressed by the formula $C^2 H^4 N$. The name points to the composition of this base, which may be regarded as a conjugate compound of ammonia with formyle, $C^2 H^4 N = NH^3 + C^2 H$. From its composition, it is evidently the simplest organic base*.

When caffeine is sublimed, it diffuses a peculiar odour ; this is far more intense on heating the double salt of formyline, and strongest when the salt is mixed with lime; at the same time a large quantity of ammonia is disengaged.

If we compare the composition of caffeine, $C^{16} H^{10} N^4 O^4$, with that of formyline and of amalic acid, $C^{12} H^7 N^2 O^8$, we find three-fourths of the nitrogen and seven-eighths of the carbon of the caffeine in these products. 2 equivs. carbon and 1 equiv. nitrogen, or the elements of cyanogen, have been eliminated. The origin of these products is explained, therefore, simply by the caffeine being resolved with the elimination of 1 equiv. cyanogen and assimilation of 1 equiv. water and 3 equivs. oxygen into formyline and amalic acid, as shown by the following equation :—

$$\underbrace{C^{16} H^{10} N^4 O^4}_{\text{Caffeine.}} + 3O + HO = \underbrace{C^2 N}_{\text{Cyanogen.}} + \underbrace{C^2 H^4 N}_{\text{Formyline.}} + \underbrace{C^{12} H^7 N^2 O^8}_{\text{Amalic acid.}}$$

That cyanogen really exists in caffeine, is proved by its behaviour towards alkalies. Caffeine, when heated with concentrated solution of potash or with soda-lime, furnishes cyanide of potassium or cyanide of sodium, and disengages prussic acid on the addition of an acid. Quinine, cinchonine, morphine and piperine, yield not a trace of cyanogen by similar treatment. It is evident that the above-mentioned volatile substance, which so much irritates the eyes, is the product of the action of the chlorine upon the cyanogen of the caffeine at the moment when the cyanogen is separated from the other elements of the caffeine. If we assume, and there are several reasons in favour of the assumption, that the formyline pre-exists in the caffeine, then we obtain for the latter the following rational formula—

* The base petinine described by Anderson, $= C^8 H^{10} N$, may be viewed as $C^8 H^7 + NH^3$, the ammonia compound of butyryle. Perhaps there will be found to exist a series of bases running parallel with the fatty acids.

$$C^{16}H^{10}N^4O^4 = Cy + [C^2H^4N + C^{12}H^4N^2O^2] + 2Aq.$$

The cyanogen appears to be contained in the caffeine in the same state as in the cyanide of aniline. The action of chlorine, or of other oxidizing agents, would simply consist in a salt of formyline being formed, the cyanogen being separated, and the group $C^{12}H^4N^2O^2$ being converted into amalic acid, with assimilation of water and oxygen.

Amalic acid is likewise produced when theobromine is treated with chlorine. If we admit $C^{12}H^4N^2O^2$ likewise in theobromine, its formula becomes—

$$C^{14}H^8N^4O^4 = C^{12}H^4N^2O^2 + \underbrace{C^2H^4N^2O^2}_{\text{Urea.}}$$

Caffeine and theobromine would therefore contain the same group of elements, $C^{12}H^4N^2O^2$, which I shall denote by $\times$ combined in theobromine with the elements of urea, and in caffeine with formyline and 1 equiv. cyanogen and 2 equivs water, or what is the same thing, with the elements of oxamide.

This relation appears still more simple, when we consider that urea may be regarded as the binamide of carbonic oxide, whilst oxamide is the amide of carbonic oxide; and formyline may be considered the amide of C^2H^2, or as oxamide, in which the oxygen is replaced by hydrogen. If $C^{12}H^4N^2O^2 = \times$, then the formula of theobromine $= \times + C^2O^2, 2NH^2$, and that of caffeine $= \times + C^2O^2, 1NH^2 + C^2H^2NH^2$. How far this connexion between caffeine and theobromine exists, will be seen from the results of an investigation which I have undertaken on the constitution of theobromine.

I may here mention that the formula of amalic acid, alloxan being $C^8H^3N^2O^9 + 1$ aq, and alloxantine $= C^8H^3N^2O^8 + 1$ aq $+ HO$, may be regarded as $C^8H^3N^2O^6 + C^4H^3O + HO$, which would explain its reactions resembling those of alloxan and alloxantine.

I must now return to the results of my researches on the caffeotannic acid of the coffee-berries and the leaves of *Ilex Paraguayensis*, on viridic acid, the lime-salt of which imparts to coffee-berries their green colour, and on the boheic acid of tea-leaves. The composition of these acids is expressed by the following formulæ:—

Caffeotannic acid	$C^{14}H^8O^7$
Viridic acid	$C^{14}H^7O^8$
Boheic acid	$C^{14}H^6O^8$

In my paper on caffeotannic acid, I have stated that it behaves like a true aldehyde. The viridic acid, which is formed from this aldehyde, has, like formic acid, the property of reducing salts of silver in a high degree. From the investigation of Liebich, it results that the acid $C^{14}H^8O^7$ passes in the presence of potash and oxygen into $C^{12}H^6O^5$, $C^{12}H^5O^6$, and lastly into $C^{12}H^4O^7$. If we bear in mind the signification of these formulæ, it will appear more than probable that these acids have the following constitution: the acid of the coffee-berries and of the leaves of Paraguay tea is a conjugate compound of $C^{12}H^6O^5$ with the aldehyde of formic acid, viridic acid

is a conjugate compound of $C^{12} H^6 O^5$ with formic acid, and boheic acid is a conjugate compound of $C^{12} H^6 O^5$ with oxalic acid, as the following formulæ show—

Caffeotannic acid..... $C^{14} H^8 O^7 = C^{12} H^6 O^5 + C^2 H^2 O^2$
Viridic acid ..... $C^{14} H^7 O^8 = C^{12} H^6 O^5 + C^2 HO^3$
Boheic acid ..... $C^{14} H^6 O^8 = C^{12} H^6 O^5 + C^2 O^3$

All the acids therefore which occur in plants capable of producing caffeine, contain the same group, $C^{12} H^6 O^5$, together with a member of the formyle series, or of the nearly related oxalic acid.

We also find in caffeine a group which contains 12 C; it has evidently been formed from the group $C^{12} H^6 O^5$ by 2 equivs. ammonia and 5 equivs. oxygen being appropriated, and 8 equivs. water eliminated, two of which remain with the caffeine, $C^{12} H^6 O^5 + 2NH^3 + 5O = C^{12} H^{12} N^2 O^{10} = [C^{12} H^4 N^2 O^2 + 2\,aq] + 6\,aq.$

The second group, the member of the formyle series, is also found in caffeine in the form of formyline and cyanogen. The elements of ammonia have taken the place of the oxygen of formaldehyde, formyline $= C^2 H^4 N = C^2 H + NH^3$. The production of the cyanogen is explained in the same simple manner; every chemist knows that cyanogen, hydrogen and water, or formic acid and ammonia, further, oxalate of ammonia or oxamide, and water or cyanogen and water are equivalent terms; they may be readily prepared from each other, and again converted into each other. 1 equiv. formic acid and its aldehyde + 2 equivs. ammonia contain the elements of formyline and of oxamide, or of cyanogen and water, $C^2 H^2 O^2 + C^2 HO^3 + 2NH^3 = C^4 H^9 N^2 O^5 = C^2 H^4 N + C^2 O^2, NH^2$ or $C^2 H^4 N + Cy + 2aq$ and of 3 equivs. water. It appears therefore to be proved from this examination of caffeine, and of the acids of the caffeine plants, that the nitrogenous substances are formed from the non-nitrogenous by the assimilation of the elements of ammonia with the simultaneous absorption of oxygen, or, without this, with the elimination of water. It is moreover evident that the more complex atoms are formed by extremely simple compound atoms being added to the substances already formed. Plants have the property of absorbing carbonic acid and water, and of separating oxygen. If a plant absorbs carbonic acid and water in the proportion of 2 : 1, and separates 1 or 2 equivs. oxygen, formic acid or oxalic acid is produced, $C^2 O^4 + HO = C^2 HO^5$ $C^2 H^2 O^5 - O = C^2 HO^4 = C^2 O^3 + aq$ oxalic acid, $C^2 HO^5 - O^2 = C^2 HO^3$ formic acid.

Now these simple products, being added to others already formed, produce the more complex atoms; the caffeotannic, boheic and viridic acids are generated by formic acid, its aldehyde or oxalic acid uniting with the already formed group $C^{12} H^6 O^5$ to form conjugate compounds.—Liebig's *Annalen*, July 1849.

On the Action of Potash upon Caffeotannic Acid.
By Gustave Liebich.

The action of potash upon caffeotannic acid having never been examined, I was induced to make it the subject of my investigation.

For this purpose I prepared pure caffeotannic acid in the following manner:—The alcoholic extract obtained by boiling coffee-berries was precipitated with an alcoholic solution of acetate of lead. The precipitate, well-washed and decomposed with sulphuretted hydrogen, furnished the caffeotannic acid, which, after expelling the sulphuretted hydrogen, was freed from every trace of foreign ingredient by repeated treatment with strong alcohol.

This acid, after being concentrated by quick evaporation, was mixed with pure potash until it showed a distinct alkaline reaction, and then exposed to the air for eight days. The liquid, which had assumed a brown colour immediately after the neutralization with potash, had in this time become much darker and opake. The lead salt, obtained from a portion of the acid by precipitation with acetate of lead after previous neutralization with acetic acid, was carefully washed and dried, and used for analysis. The following are the results:—

Carbon.....	28·42	28·64	28·73	72=5400·0		28·4
Hydrogen	1·90	2·14	2·20	32	400·0	2·1
Oxygen	18·36	17·87	18·09	34	3400·0	17·9
Oxide of lead	51·32	51·35	50·98	7	9761·5	51·4

the most simple expression for which is $4(C^{12}H^5O^6, PbO) + 2C^{12}H^6O^5, 3PbO$.

This formula shows that the action of the oxygen upon the caffeotannic acid in the presence of potash was not completely terminated. It had already passed one stage, but had not reached the second.

The lead salt was therefore prepared from the other portion of the liquid, which had been exposed eight days longer to the air. The colour of the salt, which was light brown in the first preparation, was now almost blackish-brown, proving distinctly that the oxidation had gone further, which was confirmed by the analysis:—

Carbon.....	21·51	21·27	21·21	72=5400·0		21·3
Hydrogen	1·60	1·48	1·45	24	300·0	1·2
Oxygen	16·64	16·97	16·86	42	4200·0	16·7
Oxide of lead	60·24	60·28	60·49	11	15339·5	60·8

The simplest expression is $5(C^{12}H^4O^7, 2PbO) + C^{12}H^4O^7\,PbO$, —a mixture of a basic with a neutral salt of an acid, $C^{12}H^4O^7$.

If we compare this formula with that of caffeotannic acid, it is seen that the atom of the caffeotannic acid separates in the above treatment, and that one group of atoms, $C^{12}H^6O^5$, is set free, which gradually exchanges its hydrogen for equivalents of oxygen, $C^{12}H^6O^5$, passing into $C^{12}H^5O^6$, and finally into $C^{12}H^4O^7$.—Liebig's *Annalen*, July 1849.

Examination of the Horn of Oxen. By F. Hinterberger.

Horn is one of those tissues of the animal body which has hitherto been but partially examined. Berzelius describes the behaviour of

horn towards acids and alkalies, and devotes a long chapter to horn-potash. According to him, horn is altered fibrine; he was, however, not acquainted with any analysis of it. Scherer has made us acquainted with the per-centage composition of cow and buffalo horn, for which Mulder proposed the formula $2(C^{40}\,H^{31}\,N^{5}\,O^{14}\,S) + NH^{2}$; the latter chemist likewise gives the analysis of a combination of horn with chlorine, which is said to be formed when chlorine is passed into water in which horn is suspended.

The object of the present investigation was to establish the per-centage composition of horn, and to become acquainted with those products which it furnishes on treatment with acids and alkalies. In order to submit ox horn to analysis, it is above all things requisite to prepare it pure and in as fine a state of division as possible. For this purpose I selected a very clean and dry horn of an ox, filed away the outer layers with a coarse file, and then with a fine file obtained from different parts of the horn fine powder, which was exhausted with æther and alcohol. The horn-filings, freed by exhaustion with æther and alcohol from a small quantity of fat, a small quantity of another brownish substance which was not further examined, and a trace of salts, were now suspended in a large quantity of distilled water; when the coarser powder, as well as the particles of iron removed from the file, quickly fell to the bottom, whilst the horn powder floating in the liquid was collected on a filter, dried first in the air, and then in the water-bath at 212°. On incineration, it left 1·9 per cent. ash, consisting of chloride of magnesium, chloride of sodium, phosphate of lime, peroxide of iron and silica. The combustion was made with chromate of lead and a current of oxygen; the nitrogen was determined according to Will and Varrentrapp's method. The following are the results obtained:—

Carbon	50·46	50·83	
Hydrogen	6·65	6·68	
Nitrogen	..	..	16·23
Oxygen ..... Sulphur	26·66	26·26	

As these results agreed with the analyses of other chemists, I immediately passed on to the study of the

Action of very dilute boiling Sulphuric Acid upon Horn.—For these experiments I employed the fine shavings obtained in the smoothing of combs by the comb-maker. 2 lbs. (2 parts) of concentrated sulphuric acid were added to 6 lbs. (6 parts) of spring water in a large flask, well mixed with a glass rod, and then $\frac{1}{2}$ a pound ($\frac{1}{2}$ a part) of horn shavings added, and boiled for three days continuously on a sand-bath, restoring every now and then the evaporated water. After this thirty-six hours' boiling, recently prepared milk of lime is added to it until it shows a strongly alkaline reaction, the precipitate is boiled with the liquid for twenty-four hours in an iron vessel, and the contents then poured at once into a large linen bag, and the residue expressed. The united liquids, obtained by filtration and by pressure, are boiled in an iron pot, and

dilute sulphuric acid added to the hot turbid liquid until it has a slightly acid reaction, then filtered; acetate of lead, to which some basic acetate has been added, mixed with the filtered solution until the excess of sulphuric acid is combined with lead; it is then boiled, filtered, and sulphuretted hydrogen passed through the liquid. The precipitated sulphuret of lead is heated with the liquid, filtered, and the slightly-coloured solution evaporated till it shows a crystalline pellicle. The crystals, which form after twelve hours' standing, are separated by filtration from the mother-ley, which is further concentrated; and when more crystals form, they are brought upon a filter like the former ones. The crystals so obtained are strongly pressed between blotting-paper, washed with alcohol of 0·845, and then with a little water; and are now boiled with a very little caustic potash, carbonate of potash and water; the separated carbonate of lime removed by filtration, and the liquid mixed with acetic acid until it exhibits a slightly acid reaction. When perfectly cold, the separated crystals are collected on a filter, pressed, dissolved in boiling water, and left to crystallize spontaneously. Concentrically-grouped needles separate, which are obtained perfectly white by dissolving them in boiling water, adding animal charcoal, boiling for a few minutes, and then filtering. The crystals still contained some inorganic substance; they must therefore be again dissolved in hot water, and left to spontaneous crystallization. The crystals fill the whole of the liquid, but require a very small filter, and shrink very much together in drying in the air.

In the air-dried state they form an adherent silky mass, consisting of long superposed needles, which are themselves formed of numerous minute stellately-grouped needles. They burn on platinum without residue, diffusing an odour of burnt hair; are insoluble in æther and absolute alcohol; very sparingly soluble in cold, pretty soluble in boiling water, and very readily soluble in alkalies and mineral acids. They separate unaltered from a solution in ammonia on spontaneous evaporation, but in larger crystals. The crystals, dried at 212°, furnished the following results:—

Carbon	59·85	59·17	59·06	18	108	59·67
Hydrogen	6·25	6·23	6·25	11	11	6·08
Nitrogen.....	7·89	7·87	..	1	14	7·73
Oxygen	..	..	..	6	48	26·52

The numbers correspond to the formula which Warren de la Rue advanced for the crystalline substance which he discovered in cochineal, and considered identical with the tyrosine from caseine, $C^{10}H^{11}NO^6$.

The form of the crystals and their chemical properties agree with those described by Liebig for the tyrosine from caseine, and by Bopp from that procured from fibrine and albumen. There is therefore no doubt that this substance is identical with the tyrosine discovered by Liebig, as well as with the substance procured from cochineal. Liebig advanced a different formula for tyrosine; the calculated per-centage composition, however, of which differs very little from that above given.

In general, wherever tyrosine has been found, leucine has likewise been met with; this induced me to search for the latter substance. If leucine, as is usually the case, were formed in larger quantity than the tyrosine by sulphuric acid from horn, it ought to be contained in the mother-liquor of the tyrosine; but it was not there. I consequently felt induced to believe that either it had not been formed, or had been retained in one of the lead precipitates. I now avoided the latter by slightly modifying the process. The horn was boiled with sulphuric acid; the latter precipitated as above with milk of lime, boiled, and then the excess of lime precipitated accurately by sulphuric acid. The slightly-acid filtered solution furnished on evaporation an abundant crop of crystals; and when these were removed, the mother-liquor again deposited crystals on concentration; but they were not like the first, which were spherical, whilst these had more the appearance of plates. After I had assured myself that the spherical crystals consisted almost entirely of tyrosine, I proceeded with the examination of the laminar crystals. They were pressed between numerous folds of blotting-paper, the adherent brown mass removed by washing with a little absolute alcohol, then dissolved in a little hot water, the crystals of tyrosine which separated on cooling removed, and the mother-liquor further evaporated. The crystals which now separate are nearly pure leucine, but are not quite white. They are dissolved in water, some hydrated oxide of lead added, the excess of lead removed from the liquid by sulphuretted hydrogen, and the filtered solution evaporated. The leucine thus obtained is now free from tyrosine, and can be procured of a dazzling white colour by recrystallization from water, treatment with animal charcoal, and recrystallization. It separates in nacreous plates, which are frequently deposited in concentric groups, volatilize when heated gently in a glass tube, and fly about in the air as flakes, like oxide of zinc. By this behaviour, and in part by the great solubility in water, acids and alkalies, leucine is not to be mistaken. I had too little pure substance to make an analysis of it.

The amount of tyrosine and leucine which is obtained from horn according to the above process increases within certain limits with the duration of the boiling with sulphuric acid, and perhaps also with the longer action of the milk of lime upon the sulphuric solution of the horn; for on boiling the horn only for a day with the sulphuric acid, and allowing the milk of lime to act only so long as a strong smell of ammonia was given off, as Bopp did with fibrine, albumen and caseine, I obtained but very little of these two crystalline substances. The mixture of sulphuric acid and water begins to boil at 225°, and the ebullition goes on very quietly if a few fragments of charcoal are thrown into the boiling liquid, and if, after the horn is boiled for a day with sulphuric acid, the sediment of sand and gypsum deposited during the night is removed by decanting the liquid into another glass flask. The liquid obtained after three days' boiling is of a light brown colour; when recently-prepared milk of lime is added in excess to it, a very large quantity of am-

monia is disengaged. The latter can also be detected after two days' boiling by the fumes formed on holding a glass rod moistened with muriatic acid over it; but it cannot be perceived by the smell. Along with the ammonia there is a very intense odour, which calls to mind that diffused in filing and sawing bones when they become heated. The precipitate thrown down by milk of lime is very bulky, and must be well pressed to avoid loss.

Whilst with albumen, fibrine and caseine, leucine is predominant, and tyrosine occurs but in comparatively small quantity, precisely the reverse obtains with horn; here tyrosine forms the chief constituent. 5 grms. of air-dried pure tyrosine are obtained by treating a pound of horn with sulphuric acid. The crystalline substance discovered by Bopp in the syrupy mother-liquor from the preparation of leucine and tyrosine from albumen, caseine and fibrine, has not occurred to me in the examination of horn; this syrupy liquor becomes less the longer the sulphuric acid is left in contact with the horn.

It being known from previous experiments that tyrosine and leucine are likewise produced by fusing fibrine, albumen and caseine with hydrate of potash, it appeared highly probable that this would also be the case with horn. Experiment confirmed the supposition. Horn shavings were fused in a large iron pot with an equal weight of hydrate of potash until hydrogen was given off along with the ammonia, and the brown colour of the liquid mass had become lighter; it was then dissolved in boiling water, acetic acid added until it was faintly acid, filtered, and the solution evaporated to crystallization. After twelve hours a pretty considerable quantity of tyrosine had separated and a little leucine; they were separated as above.

When the aqueous solution of the fused mass is supersaturated with sulphuric instead of with acetic acid, and submitted to distillation, a product with the odour of human fæces and of an acid reaction is obtained, which is somewhat milky from the presence of white flakes, and becomes yellowish-red by exposure to the air. When this distillate is saturated with barytic water, on repeating the distillation the acids are left in the retort combined with the baryta, whilst a neutral, stinking, clear liquid passes over. The residue in the retort is mixed with carbonate of soda, the precipitated carbonate of baryta removed by filtration, and the liquid evaporated to dryness in the water-bath. When these soda salts are distilled with sulphuric acid, acetic acid and some oily acids pass over. To separate the former from the latter, the distillate is divided into two portions, one-half saturated with carbonate of soda, and the other poured back to the neutralized half. At present oily acids pass over, and only a little acetic acid. Now if this distillate is divided, like the first, into two equal parts, and the one is again saturated with carbonate of soda in a retort, and the still acid portion added, and again distilled, only the oily acids now pass over, and the residue in the retort consists solely of acetate of soda. The oily acids, evaporated to dryness with soda, and then decomposed with sulphuric

acid, furnished distinctly the odour of butyric and valerianic acids.

Sulphuric acid and hydrate of potash produce therefore from horn leucine and tyrosine, and the latter in such comparatively large quantity, that it would be the most advantageous method of preparing tyrosine for a more accurate examination of this substance. —Liebig's *Annalen*, July 1849.

On the Oxides of Cobalt. By C. Rammelsberg.

The combinations of the protoxide of cobalt, CoO, with oxide of cobalt, $Co^2 O^3$, have been examined by Winkelblech and Beetz. The compound $Co^3 O^4$ or $CoO, Co^2 O^3$, which consists of 73·46 cobalt and 26·54 oxygen, is obtained when the oxide $Co^2 O^3$ or its hydrate is heated.

The compound $Co^6 O^7$, or $4CoO + Co^2 O^3$, which contains 75·98 per cent. of metal to 24·02 oxygen, is formed when either cobalt, the protoxide, the carbonate or the oxalate of the protoxide, is heated in the air. According to Beetz, it is so stable that it may be employed for the estimation of cobalt.

Rammelsberg has made a long series of experiments on this subject, and has found that this oxide is by no means adapted for the estimation of cobalt; it must be reduced by hydrogen. For these experiments, solutions of pure cobalt were precipitated, some by hydrate of potash, some by carbonate of soda, at a boiling temperature, and from acetate of cobalt the protoxalate thrown down by oxalic acid, and the precipitates ignited, some in the air and some in oxygen. The amount of metal was subsequently determined by ignition in hydrogen.

The hydrate of the protoxide of cobalt, precipitated by a solution of potash, and heated in a platinum crucible over an Argand lamp, contained 74·28 per cent. of metal.

The protocarbonate of cobalt, treated in the same manner, furnished 72·69, 73·63, 73·65, 74·27, 74·44 per cent. of metal.

The oxalate of the protoxide of cobalt, calcined in the air, contained 73·62 per cent. of metal; heated in oxygen, it furnished 73·68, 73·83 and 74·33 per cent. of metal.

All these compounds therefore had become converted by ignition into the compound $CoO, Co^2 O^3$. This result differs from those obtained by Winkelblech and Beetz. Winkelblech found, on heating the hydrated protoxide in a platinum capsule in the air until the weight remained unaltered, a compound containing 75·625 and 76·133 per cent. of metal, and Beetz found 75·77 per cent., whilst he obtained from the compound prepared by calcining the carbonate 75·85 per cent. cobalt. Both chemists therefore had under their examination $Co^6 O^7$; whilst Rammelsberg, undoubtedly owing to the use of a lower temperature, obtained the compound $CoO, Co^2 O^3$, which agrees with the earlier statements of Hess.

This oxide however is not formed only from the protoxide and its compounds, but also from the hydrate of the oxide when it is cal-

cined. This is evident from the experiments of Hess, who found in it 73·92 per cent. of metal, and of Beetz, who obtained 72·83 and 73·15 per cent. of metal. Rammelsberg has also examined the residue on calcining the hydrate of an oxide which had been prepared by treating the precipitate thrown down by carbonate of soda from a solution of the acetate of the protoxide with chlorine, and purifying the black oxide with cold dilute nitric acid. 100 parts of the compound, calcined in the air, left on reduction 72·96 and 73·42 per cent. of metal.

Rammelsberg has on this occasion made several determinations of the specific gravity of metallic cobalt and nickel, and of the protoxide of cobalt and the protoxide of nickel, which are arranged below for the sake of comparison with the determinations of other chemists.

A. contains the results found by Rammelsberg for metallic cobalt reduced in hydrogen, and B. for the protoperoxide of cobalt, $CoO + Co^2 O^3$:—

A. Co.	Fused metal.	B. $CoO, Co^2 O^3$.
8·132	8·485 according to Brunner.	5·833
8·643	8·513 according to Berzelius.	6·090
9·138	8·538 according to Tassaert and Hauy.	6·296
9·375	8·700 according to Lampadius.	6·073 = mean.
9·495		
8·9566 = mean.		

For metallic nickel reduced by hydrogen, the author found 8·975 and 9·261; mean, 9·118. The protoxide of nickel gave 6·661. The following are the statements for fused nickel :—

Reduced *per se* in the porcelain furnace	8·279 according to Richter. 8·402 according to Turte.
From oxalate fused under a layer of glass	8·673 according to Brunner.
Hammered	8·666 according to Richter. 8·932 according to Turte.
Reduced in a charcoal crucible.....	9·000 according to Vauquelin and Hauy.

Poggendorff's *Annalen*, lxxviii. p. 93.

On a Product of the Action of Nitric Acid upon Woody Fibre. *By* J. A. Porter.

In a paper recently published, M. Sacc* mentions as a product of the action of nitric acid upon woody fibre, pectic acid. This truly remarkable phænomenon, that a substance owing its origin to the action of so powerful an oxidizing agent as nitric acid, should, when once prepared, be readily altered by the same acid, rendered it desirable that a comparison should be made between the substance

* Chem. Gaz. p. 274 of the present volume.

obtained by means of nitric acid from woody fibre, and pectic acid procured according to the usual methods from roots or fruits.

200 grms. of deal sawdust were heated for several hours with 2 kilogrammes of commercial nitric acid and 400 grms. of water, and the white pasty mass obtained washed with distilled water. M. Sacc found that the substance procured in this manner dissolved entirely in dilute ammonia; and it was this substance which, after drying at 212°, he submitted to analysis. The substance which I obtained, according to this process, was not perfectly soluble in ammonia, but left a trace of a body of syrupy consistence upon the filter. The entire mass was therefore treated with dilute ammonia, the solution filtered and precipitated with muriatic acid. After being perfectly dried at 212°, this precipitated substance had a slight reddish-gray colour. In order to compare it with pectic acid, I prepared some of the latter, according to Chodnew's method*, from turnips. In the course of preparation some difference was perceived; the pectic acid from the turnips becoming fibrous on washing in alcohol and pressing in the hand, whilst that obtained from the wood retained its mucilaginous consistence. Both substances were, moreover, compared after being dried at 212°.

Pectic acid was somewhat soluble in boiling water, and an addition of sugar or of alcohol caused coagulation. The substance procured from wood was insoluble in boiling water.

Pectic acid dissolved readily in alkalies, from which, by the addition of acids, it was precipitated in the form of a perfectly transparent jelly. The other substance dissolves with difficulty in alkalies, and the gelatinous precipitate rapidly aggregates into white transparent flakes. From its solution in concentrated alkalies it is separated as a light white powder, which is not the case with pectic acid. The solutions of both substances in alkalies were thrown down by alcohol; and on boiling with strong alkalies, both substances lost after some time the property of being again precipitated from the solution by acids. I could detect no remarkable differences in the behaviour of the alkaline solutions of the two substances towards metallic solutions. The precipitates with solutions of silver, lead and copper, for instance, have the same appearance. Both substances impart a red colour to muriatic acid when boiled with it. Sulphuric acid blackens both the substances with evolution of the smell of burnt sugar.

Towards moderately dilute nitric acid the two substances exhibit a different behaviour; pectic acid furnishes mucic acid, which on cooling separates as a white crystalline powder from the solution, and is readily recognized by its insolubility in alcohol and sparing solubility in cold water. As is well known, Fremy obtained mucic acid from pectic acid by oxidation with nitric acid; while Chodnew could obtain none, probably from his employing a more concentrated nitric acid. The substance prepared from wood is gradually converted into oxalic acid on ebullition with nitric acid of the same strength, without the liquid depositing crystals on cooling.

* See Chem. Gaz. vol. iii. p. 127.

For further comparison, I submitted the substance prepared from wood to analysis. It was previously dried at 212°, finely pulverized, and then kept at 212° until no decrease in weight was perceptible. It contained 0·37 ash, not a trace of nitrogen, and :—

Carbon	43·38	43·64	43·16	16 =	96	43·63
Hydrogen.....	5·84	5·97	5·78	12	12	5·45
Oxygen.....	50·78	50·39	51·06	14	112	50·92

If we attempt to express the results of these analyses by a formula, we obtain as the most probable $C^{16} H^{12} O^{14}$. This formula, compared with that recently advanced by Fremy for pectic acid, $C^{16} H^{11} O^{15}$, contains one equiv. hydrogen more and one equiv. oxygen less. The results which M. Sacc obtained in the analysis of the substance prepared from wood, according to the same process, were—

Carbon	40·83	42·10	42·82	14 =	42·00
Hydrogen..	5·86	6·00	5·94	12	6·00
Oxygen....	53·31	51·90	51·20	13	52·00

These results differ essentially from each other, especially in the amount of carbon; so that the formula adopted by M. Sacc cannot exactly be considered as the expression of the analytical results.

The reasons which led M. Sacc to regard the substance prepared by him from wood as pectic acid were,—1st, its appearance; 2nd, its ready solubility in the moist state in ammonia; and 3rd, its being precipitated by acids from that solution as a transparent jelly. From the results of my examination, the substance procured by the action of nitric acid upon wood cannot be looked upon as pectic acid, although it is very closely related to it. The reasons which lead me to this view are,—1st, the different behaviour of the two substances towards alcohol; 2nd, the insolubility of the substance from wood in boiling water; 3rd, the different appearance of the precipitate from a solution in excess of potash; 4th, the substance prepared from wood furnishes no mucic acid when boiled with nitric acid. Lastly, the composition found by me does not agree with that of pectic acid.—Liebig's *Annalen*, July 1849.

On Sulphocyanide of Benzoyle and its Products of Decomposition. *By* B. Quadrat.

When crude oil of bitter almonds or pure hydruret of benzoyle is mixed with sulphuret of carbon and ammonia, two strata are formed, the lower one of which contains the whole of the oil of bitter almonds. At the surface of contact of the oil and of the mixture of sulphuret of carbon and ammonia, a red colour is produced by the formation of Zeise's salt. The upper stratum subsequently becomes red throughout, and a yellow resinous substance separates upon its surface. When an acid is poured over the red liquid, sulphuretted hydrogen is given off and the above-mentioned yellow body separates; it is soluble in caustic potash, from which solution

it is precipitated by acetic acid. The lower stratum becomes milky, and in the course of two or three days distinct crystals are formed at the bottom and on the sides of the vessel. When the crystals are left for a long time in the liquid, they gradually disappear; the same effect is also produced by oil of bitter almonds. The mother-ley is poured off by inclining the vessel, and the crystals freed for the greater part from adherent undecomposed oil of bitter almonds by pressure between paper, and are afterwards washed upon a filter with æther. The prismatic crystals are colourless, but in general crystalline granules are obtained. They dissolve in alcohol and æther, but not without decomposition. The ætherial solution deposits on evaporation slender acicular crystals. When left long exposed to the air, they give off a peculiar odour and become yellow; they have a bitter taste, and are very quickly decomposed at 212°.

For analysis, the substance was dried for several weeks *in vacuo*. The carbon was determined by combustion with chromate of lead, with the addition of copper turnings; the sulphur could not be estimated by means of nitric acid, because the heat which is evolved by the reaction of the acid upon the substance volatilizes a portion unoxidized. The total amount of the sulphur may be oxidized by heating the substance in a platinum dish with caustic potash and nitre, or with carbonate of baryta and nitre. For the estimation of the nitrogen, the substance was burnt with soda-lime. The hydrogen was calculated from the loss at 3·87 per cent.; for this reason, that the hydrogen determination of sulphurous bodies according to the usual method is defective. The water formed in the combustion had always an acid reaction; the error however is rendered very small when superoxide of lead is inserted in the combustion-tube itself. The following are the per-centage results:—

Carbon	65·12	65·10
Hydrogen	3·87	
Nitrogen.....	9·4	
Sulphur	21·88	21·61

The Decomposition by Perchloride of Iron explains satisfactorily the grouping of the elements. When a solution of perchloride of iron is mixed with the substance, the liquid acquires a blood-red colour, and an oily liquid distils over on the application of heat. The blood-red colour arises from the production of sulphocyanide of iron, and the oil has the composition and all the properties of the oil of bitter almonds. The following decomposition occurs:—

$$3(C^{16}H^5NS^2)+Fe^2Cl^3+6HO=Fe^2(CyS^2)^3,3ClH,3(C^{14}H^6O^2).$$

The compound $C^{16}H^5NS^2$ is consequently sulphocyanide of benzoyle, in which the sulphocyanogen and benzoyle can readily be detected. If we regard the oxide of benzoyle discovered by Ettling to be according to its composition, $C^{14}H^5O^2$, then the sulphocyanide of benzoyle is its cyanogen compound, in which the oxygen is replaced by sulphur.

Decomposition by Alcohol.—When the sulphocyanide of benzoyle is boiled with nearly absolute alcohol, hydrosulphate of ammonia and

carbonic acid are evolved, and the liquid assumes a yellow colour. On cooling, white laminæ separate, which were freed from mother-liquor by washing with absolute alcohol. The substance was dried under the air-pump without experiencing the least decomposition; it furnished on analysis—

Carbon	71·80	71·53	56	71·80
Hydrogen	5·20	5·30	24	5·13
Nitrogen	5·90	5·80	2	5·98
Sulphur	17·77	17·49	5	17·10

This body is formed from the sulphocyanide of benzoyle according to the following equation:—

$$4(C^{16}H^{5}NS^{2}) + 12HO + O^{4} = C^{56}H^{24}N^{2}S^{5}; 2NH^{3}; 2SH, 8CO^{2}, S.$$

The sulphur is retained in solution by the hydrosulphate of ammonia.

The occurrence of the above products of decomposition may be clearly demonstrated by arranging the experiments so that the volatile products first pass through a solution of protosulphate of iron and then into baryta water. The absorption of oxygen was proved by direct experiment.

The grouping of the several elements will be more clearly seen from the following:—

$$2(C^{14}H^{5} + NH^{2}S^{2}) + 2(C^{14}H^{5}) + S.$$

$C^{14}H^{5} + NH^{2}S^{2}$ is benzamide, the O of which is replaced by S.

Decomposition by Ammoniacal Alcohol and Water.—A hot solution of the sulphocyanide of benzoyle in alcohol of 0·951 spec. grav., to which some ammonia is added, furnishes, on the addition of so much water that a permanent milkiness is produced, a crystalline powder on cooling, which it is difficult to separate from the mother-liquor. It is insoluble in water, and its alcoholic solution is decomposed, on which account it is not possible to recrystallize it. The substance dried *in vacuo* gave the following analytical results:—

Carbon	72·00	56	71·49
Hydrogen	5·78	26	5·53
Nitrogen	6·60	2	5·95
Sulphur	16·76	5	17·03

The elements are probably grouped as follows:—

$$C^{14}H^{5}(NH^{2})S$$
$$C^{14}H^{5}(NH^{2})$$
$$2(C^{14}H^{6}S^{2}).$$

Decomposition by Heat.—When the sulphocyanide of benzoyle is heated in a retort in the oil-bath, it melts with tumescence at the boiling-point of water, and begins to be decomposed; at 248° sulphuret of carbon and ammonia escape, and a portion of undecomposed oil of bitter almonds distils over into the receiver. Scarcely are these products of decomposition eliminated, when they react upon each other and acquire a red colour owing to the production of Zeise's salt. At this temperature the odour of benzole becomes

perceptible. At 302° the frothing yellowish contents of the retort suddenly become liquid, the disengagement of gas ceases, and the liquid begins to boil between 410° and 428°. The small quantity of substance which passes over congeals in the neck of the retort to a mass of minute acicular crystals. If the operation is discontinued at this temperature, the mass on cooling appears as a yellowish resinous substance, in which are diffused slender acicular crystals; it is separated into two constituents by the addition of alcohol of 0·951 spec. grav., one of which remains suspended in the alcohol, whilst the other dissolves in it. The substance collected on the filter is crystalline, insoluble in water, and very slightly soluble in alcohol: it is not decomposed at 212°, and is not altered by nitric acid. On analysis it furnished—

Carbon	82·54	82·51	15	82·57
Hydrogen	5·26	4·99	5	4·59
Nitrogen	12·53		1	12·85

Laurent has examined a substance, benzoyle-azotide, with the following results :—

	Theory.		Laurent.
Carbon	81·60	14	82·03
Hydrogen	4·79	5	4·88
Nitrogen.....	13·64	1	13·08

The substance $C^{15} H^5 N$ is formed from $C^{16} H^5 NS^2$ by the separation of sulphuret of carbon; a second atom of sulphocyanide of benzoyle furnishes the other products which occur in this decomposition.

The substance $C^{15} H^5 N$ examined by me is closely related in its properties to benzoyle-azotide.

The liquid filtered from the substance insoluble in alcohol, deposits, on the addition of water, a crystalline substance. By washing with weak spirit and subsequent pressure between paper, a yellow resinous mass was obtained, which had a peculiar odour, arising from other adherent products of decomposition, and could not be obtained pure.

This investigation has made us acquainted with a series of substances, all of which contain $C^{14} H^5$, combined with different quantities of sulphur, amidogen or sulphocyanogen. The production of a sulphocyanide by the action of sulphuret of carbon and ammonia, is explained from the behaviour of CS^2 and NH^3, which, according to the experiments of Zeise, is as follows :—

$$2CS^2 + 3NH^3 + C^{14} H^6 O^2 = \underbrace{C^{16} H^7 NS^2}_{\text{Sulphocyanide of benzoyle.}} + 2NH^4 S + 2HO.$$

The sulphuret of ammonium is held dissolved in the liquid.

Amygdaline, $C^{40} H^{27} O^{22} N$, may be considered, from the products which it furnishes with synaptase, as $2(C^{12} H^{10} O^{10}) + C^{14} H^6 O^2 + C^2 NH$. It is moreover highly improbable that oil of bitter almonds and prussic acid pre-exist in amygdaline, as it does not possess all the reactions which characterize prussic acid and the oil of bitter almonds. These two substances evidently stand in a different relation to amyg-

daline from that of saligenine to salicine. Starting from the composition of the sulphocyanide of benzoyle above described, the following expression may be advanced for the rational composition of amygdaline*:—

$$C^{40}\,H^{27}\,NO^{22} = 2(C^{12}\,H^{11}\,O^{11}) + C^{14}\,H^{5}\,Cy.$$

The last member of the formula is the cyanogen compound corresponding to the sulphocyanide of benzoyle, and which, like that, is capable of being resolved by the elements of water into prussic acid on the one hand, and oil of bitter almonds on the other.

$$C^{14}\,H^{5}\,Cy + HO = C^{14}\,H^{5}\,O + Cy\,H\,;\text{ and}$$
$$C^{14}\,H^{5}\,O + HO = C^{14}\,H^{6}\,O^{2},\text{ or oil of bitter almonds.}$$

Liebig's *Annalen*, July 1849.

Analysis of Milky Blood. By MM. Chatin *and* Sandras.

The man from the vein of whose arm this blood was drawn applied in 1847 for relief to the Hospital of Beaujon. It was of a whitish colour, separating when set aside into a clot which was not buffed, and a serum resembling an emulsion, which had a yellowish tinge from containing some red blood-corpuscles in suspension.

The serum was inodorous and tasteless; it rendered very slightly reddened litmus-paper blue. Under the microscope, a large number of fatty globules, exactly resembling those of milk, were seen. Many of them were very large; others, exactly similar to these, were seen to form under the microscope by the union of smaller ones. Acids, heat and bichloride of mercury coagulated the liquid, but did not remove its opacity. When set aside in a tube, the liquid became gradually clearer at the lower part, in proportion as a white layer, which was thicker and more opake, formed upon the surface and extended downwards. When agitated with æther, the serum yielded all the fatty matter it contained to this menstruum, becoming at the same time clear. When mixed with æther under the microscope, the fatty globules were dissolved, but no albuminous membrane separated.

The ætherial solution, when spontaneously evaporated in the sun, left a yellow fatty matter resembling butter, which solidified at 79° F. When exhausted with anhydrous alcohol, this fatty matter left a residue consisting of albumen and extractive, which were separated by alcohol of 0·901. The albumen possessed its normal characters, and gave the well-known blue colour with muriatic acid. The fatty matter which was dissolved in the alcohol was mixed with that extracted by æther from the dried and powdered serum.

The dried residue of the serum, after having been exhausted with æther, was treated with alcohol which boiled at 205° F. It took up a substance which separated on cooling: this consisted of minute pearly plates, which did not fuse at 212° F., were unsaponifiable, and exhibited all the properties of cholesterine. The fatty matters

* This view has been previously suggested by Prof. Wöhler.

which had been separated by the æther exerted no action upon litmus-paper. It yielded a very minute quantity of an alkaline ash on incineration. When saponified with a hot solution of soda, a portion remained unacted upon. The latter consisted of a white shining mass, readily soluble in alcohol, which boiled at 105° F., and partly again separated on cooling; another portion was precipitated on the spontaneous evaporation of the alcohol.

The pearly mass, which was insoluble in alkalies and was taken up by the alcohol, appeared to consist of a mixture of different substances, as ten different quantities separated at various periods after each other, and fused at different temperatures. The substance consisted of a mixture of seroline and cholesterine.

The first deposit fused at 98° F.; it formed pearly flakes.

The second deposit fused at 187° F.; it consisted of very fine filamentous portions and pearly scales.

The third portion did not fuse in boiling water, and consisted of pearly scales only; the subsequent deposits also exhibited these properties. From the reaction of this mixture with soda and alcohol, and from its external aspect, it was sufficiently evident that the first substance which subsided was Boudet's seroline; the second, a mixture of this substance with cholesterine; and the third, pure cholesterine.

The soda solution of the fatty matter was treated with chloride of calcium; a solid soap then separated; the remaining liquid was treated with muriatic acid, concentrated, and mixed with twice its weight of rectified alcohol. The saline precipitate was removed, and the alcoholic solution evaporated; the residue consisted of almost pure glycerine. The soap obtained above was dissolved in the smallest possible quantity of hot water, and treated with a slight excess of neutral acetate of lead; the lead soap was washed, dried in a water-bath, and treated with æther, which dissolved the greater part of it. This ætherial solution was mixed with 8 times its volume of water, and heated until the whole of the æther had been driven off; the liquid was then treated with muriatic acid, which caused the separation of a liquid fatty acid, possessing all the properties of oleic acid.

The soap, which was insoluble in æther, was boiled with dilute sulphuric acid; a solid mass, which fused at 144° F., and possessed all the properties of margaric acid, separated on the surface.

The proportion of the fatty matters was—

Seroline	0·07
Cholesterine	1·23
Oleine	66·50
Margarine	32·20
	100·00

The fatty matters formed 6·05 per cent. of the serum of the blood.

Journ. de Chim. Méd., June 1849.

THE CHEMICAL GAZETTE.

No. CLXXII.—December 15, 1849.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Examination of the Liquid of Hydatid Cysts (Echinococci). *By* Dr. W. Heintz.

Dr. W. Heintz has made an analysis of the liquid contained in some hydatid cysts, which had formed in the liver of a woman. The quantity of the liquid which he procured amounted to about 3 pints. It was colourless, and, with the exception of a few flakes which rapidly subsided, was clear. These flakes consisted of the Echinococci or of smaller cysts. The specific gravity of the clear filtered liquid was 1·0076. It was rendered slightly alkaline by the presence of carbonate of potash and soda, contained no ammonia, and an extremely small quantity only of albumen. It did not contain any sulphuric acid, and mere traces of phosphoric acid.

Of organic matters, kreatinine was sought for in vain by the use of solution of chloride of zinc, neither were urea, uric acid nor other definite organic substances present. The only organic compound which could be obtained from it, was the soda-salt of an acid, which, if not a new acid, appears to be succinic acid, at least it agreed with that acid in its properties, so far as the quantity of the substance admitted of comparison. It was precipitated from its solution by absolute alcohol in the same form as succinic acid from amber, in an experiment instituted for comparison. It was somewhat soluble in æther, very difficultly so in water, had a strongly acid reaction, and formed with lime a salt which was soluble in water and which fused at 356° F. When examined by Lassaigne's test, it was found to be free from nitrogen. The crystalline form of the acid from the hydatid cysts and true succinic acid after sublimation, when compared, were found to be perfectly identical.

Analysis could not be made of it, because the total quantity of acid obtained only amounted to 0·25 grm. The most advantageous method of procuring the acid from the hydatid liquid, appears to consist in evaporating the latter to a syrup, treating the residue with muriatic acid and shaking the mixture with æther. By recrystallizing the residue left by the æther after evaporation, the acid is readily obtained in a state of purity. In its quantitative analysis, in accordance with the preceding details, the inorganic constituents of the hydatid liquid alone remained to be examined, because succinic acid was the only organic substance which could be detected; the amount of this acid was determined by ascertaining the quantity of carbonate of soda which remained in the ash after incineration.

The result is only of value, provided the supposition of the absence of all other organic acids is admitted.

Excluding the traces of phosphoric acid and albumen, 1000 parts of the liquid, containing 986·76 water and 13·24 solid residue, consist of—

Chloride of calcium	0·46
Chloride of magnesium	0·20
Chloride of potassium.....	0·24
Chloride of sodium.....	3·85
Succinate of soda	3·41
Extractive matter	5·08
	13·24

Jenaische Ann. f. Physiol. u. Med., vol. ii., p. 180.

Analyses of Cast Iron. By F. C. Wrightson, Esq.*

The effect of phosphorus in producing what is termed "cold short iron" has long been admitted. That the use of the hot blast occasioned an *increase* in the phosphorus of the iron has, however, so far as I am aware, never been suspected; at all events, the fact has never been announced. It was with the view of elucidating this point, and also of furnishing more complete analyses of cast iron than had yet been done, that I undertook, in the autumn of last year, a series of analyses, the results of which I communicated to the Birmingham Philosophical Society; and they were afterwards published in No. 3 of the 'Quarterly Journal of the Chemical Society.' It is necessary to mention this for reference, the results as to phosphorus being partly deduced therefrom. I have endeavoured in the present analyses more completely to establish the fact, that the hot blast increases the "cold shortness" of iron, by occasioning the reduction of a larger amount of phosphoric acid. I have also paid some attention to the different states in which carbon appears to be combined, which I shall point out; a fact previously noticed by Bromeis and Karsten.

Karsten states, that if the ore contains phosphoric acid, he has invariably found it as phosphorus in the slag. I have appended a number of analyses of the ores from which the cast irons were made. Phosphoric acid exists in most of them to a considerable extent. They are never smelted separately, but indiscriminately, two, three or four kinds at once.

Karsten states, that the artificial graphite, obtained by dissolving gray iron in an acid, must be considered as a compound of carbon and iron. He does not, however, give any analyses of this substance. I have examined some specimens obtained by treating the irons C. I., C. III., H. VII. and H. VIII. Those of the higher numbers contain carbon and iron (besides small quantities of silica, &c.) in nearly their equivalent ratios; whilst the lower numbers appear to be mixtures of silicates of oxide of iron, &c., with varying proportions of carbon.

* Communicated by the Author, having been read before the British Association at Birmingham, September 1849.

It would seem, in fact, as though the carbon of the latter had separated from the molten iron in an uncombined state, and that of the former as a carburet. I say, "separated from the *iron*," to distinguish it from that which evidently remains *combined* in the iron, with it or other elements, or it could not be eliminated as a hydrocarbon when the iron is treated with acids; but the nature of these combinations of carbon would be an ample subject for distinct investigation. In distinguishing between the carbons existing in the specimens, I would only observe that the *b*-carbon is separated by acids, and may be collected on a filter, whilst the *a*-carbon cannot be so collected; it escapes as a hydrocarbon, having a powerful alliaceous odour, and may be partially collected as a liquid. I have only further to notice the invariable presence of sodium or potassium, or both, in these irons. Karsten states that they have not been found as constituents of iron hitherto. As they are present in only a few of the ores, they are probably, in part at least, derived from the smelting materials.

Method of Analysis for the Irons.—The specimens were easily broken to small pieces in a steel mortar. In one portion of from 20 to 30 grs. the sulphur and phosphorus were determined. In a second quantity, all the other constituents were determined except the carbon. On being treated with HCl and warmed, the iron is quickly acted on, and in a few hours dissolved, leaving black flakes and particles floating in the liquid. These were collected on a filter previously dried at 212° and weighed. After well washing, until no trace of HCl remained, the filter was again dried and weighed. The increase was carbon principally, with small quantities of silicates of oxide of iron, lime, &c., and in the numbers VII. and VIII., iron in an *equivalent* proportion to the carbon. In these latter, as also in the numbers I. and III., the silica, iron, &c. of the substance separated by the filter were determined by fusing it with nitrate of potash mixed with twice its weight of carbonate of soda; the iron, &c., separated in the usual manner, gave the carbon by loss. This was afterwards verified in two instances by a direct determination of the carbon in a combustion-tube. The iron, &c., separated in the above manner, was added to that obtained from the *solution*. The carbon was designated *b*, and being deducted from the *entire* quantity found in the iron by the method to be detailed, gave the quantity of carbon designated *a* for the reason before named. The filtered liquid and washings, evaporated to dryness and again treated with acid and water, usually left a minute portion of silica, which was separated, weighed, and added to the former quantity. A current of sulphuretted hydrogen being passed through a small quantity of the solution, it in no case gave any other than a milk-white precipitate of sulphur. After being carefully freed from this and from SH, it was returned to the main solution, NO^5 added, and boiled until all the iron was peroxidized, and ammonia added gradually until the solution only faintly reddened litmus, and nearly all the iron was precipitated. A little neutral benzoate of ammonia separated the last portions of the peroxide of iron. The precipitate,

after well washing, was dried, ignited, weighed and examined for manganese by fusion with nitrate and carbonate of potash; for chrome and alumina by dissolving in ClH, and precipitating with caustic potash in excess; only minute traces of alumina were occasionally found in the potash. But the peroxide had in one or two instances to be redissolved and the manganese separated afresh. This occurred when ammonia had been added to the solution in excess, and a few drops of HCl again added, which were not sufficient to neutralize or acidify the whole of the solution, which from being very bulky required care in neutralizing. When the entire solution, after attaining the requisite degree of acidity, was transferred from one vessel to another so as to obtain a uniform mixture, then no trace of manganese was found with the iron. From the amount of peroxide the per-centage of iron was calculated. Before proceeding to separate the manganese, the solution and washings were evaporated to dryness, and the salts of ammonia driven off by ignition to redness. This, I had found from repeated trials, was absolutely necessary, in order to separate the whole of the manganese by hydrosulphate of ammonia. After ignition, the residue was always of a brown colour from the peroxide of manganese; a drop or two of HCl dissolved this. Ammonia and hydrosulphate of ammonia were then added, and the solution allowed to stand for several hours, and gently warmed. The sulphuret of manganese thus separated was converted into sulphate of manganese, from which the per-centage of manganese was calculated. In one or two cases, where small quantities of nickel and cobalt were present, these were left as sulphurets on the filter, when the sulphuret of manganese was dissolved by dilute sulphuric acid. The solution, after getting rid of the excess of hydrosulphate of ammonia, was neutralized, and oxalate of ammonia added. The lime thus separated was converted into carbonate, and from it the proportion of calcium deduced. A drop or two of the solution with phosphate of soda occasionally indicated *very minute* traces of magnesia; these were overlooked. After separating the lime, the solution was evaporated to dryness, ignited in a platinum capsule, and the residue, consisting of the alkaline chlorides, weighed; a few drops of solution of bichloride of platinum being added to the moistened salts, the potash was separated (when sufficient in quantity to weigh) in the usual manner; the weight of the chloride of potassium calculated, and deducted from the weight of the mixed chlorides; the loss gave the weight of the chloride of sodium.

Determination of the Sulphur and Phosphorus.—The iron, reduced to fragments, was treated with fuming nitric acid and gently warmed; the reaction was violent. The nitrous fumes given off contained no trace of SH. The solution was evaporated to dryness, and the dried mass treated with HCl and water; to a little of the filtered solution a drop or two of BaCl was added; if, after standing several hours, any precipitate or cloudiness was occasioned, the whole of the solution was treated in like manner, and the sulphate of barytes allowed fully to subside, separated, detached from filter, &c., and the weight of sulphur calculated. The excess of BaCl was

separated from the solution by a few drops of dilute SO^3, and afterwards supertartrate of ammonia added in sufficient proportion to prevent the precipitation of the iron by ammonia, which was then added in considerable excess, and a current of SH passed through the solution for several hours. The solution was then allowed to stand in a warm place until it had become of a clear light yellow colour, when it was quickly filtered and washed with water containing a little hydrosulphate of ammonia. The solution was then evaporated to dryness, the ammoniacal salts driven off by ignition, and the residue, consisting of phosphoric acid, with minute portions of lime, alumina and alkalies, fused with a little carbonate of potash and soda. [This fusion sometimes required repeating once or twice before the whole of the phosphoric acid was detached as tribasic alkaline phosphates.] The PO^5 was then determined in the usual manner as the ammonio-phosphate of magnesia.

Determination of Carbon.—The iron was reduced to a moderately fine powder by being turned in a lathe. A still finer powder was obtained from this by sifting through lawn. About 30 or 40 grs. of this were rubbed for a considerable time in an agate mortar along with about its own weight of hard white sand, which had been previously mixed with a little oxide of copper, and ignited to destroy any traces of organic matter. When an almost impalpable powder was thus obtained (care being taken to avoid any loss by rubbing over a sheet of glazed paper), it was mixed with 6 or 8 times its bulk of chromate of lead, and introduced into a combustion-tube, at the extreme point of which a few grains of chlorate of potash had been placed; the combustion was conducted with the usual precautions, and the carbon calculated from the carbonic acid formed, the latter of course being passed through a CaCl tube previous to absorption. Trials were made with the substances remaining in the combustion-tube, to ascertain if any trace of carbon remained therein; but no trace of carbonic acid was obtained by attempted recombustion of substances again powdered.

Nitrogen was sought for in the iron by mixing the powder with soda-lime, &c.; but none, or only such minute traces of ammonia were obtained as to render it questionable if they might not have been derived from the atmosphere of the laboratory. I append a comparison of the proportions of phosphorus in the hot and cold blast iron, taken from this and the series of analyses before alluded to. No. V. is generally considered the best in quality for forge iron, Nos. VII. and VIII. being too brittle, this in all probability arising from the different mode in which the carbon is combined. The difference in appearance between these two irons and the others is remarkable, being of a much whiter and finer fracture, with only a few grayish specks in the centre of the "pig." In No. V. these are much increased, and the colour is of a mottled gray; in Nos. IV. and III. the colour is still darker. These different appearances can be caused in the same iron simply by altering the time of cooling; if, for example, when the iron of the gray or mottled kind is running, a portion just set be thrown into cold water, it becomes precisely similar to No. VII. or VIII.

Analyses of Seven Specimens of South Staffordshire Iron Ores.

	I. Binds.	II. Blue flats.	III. Penny earth.	IV. Gubbin.	V. White iron stone.	Also called grains. VI. White free.	VII. Black free.
Water	4·41	2·63	0·50	1·02	0·58	0·54	1·42
Organic matter		1·67	1·81	1·05	0·41	2·19	
Silica	42·82	10·15	8·18	14·57	17·00	15·35	9·01
Alumina	13·72	trace	2·40	4·91	12·92	11·19	5·99
Carbonic acid	14·79	30·82	33·36	27·06	24·51	25·79	30·10
Protoxide of iron	19·30	49·41	50·72	44·50	39·14	41·18	50·71
Protoxide of manganese	0·25	..	0·80	0·51	2·66	2·83	1·22
Protosulphuret of iron	..	..	..	..	..	..	trace
Lime	trace	2·62	1·61	1·75	0·26	0·61	1·72
Magnesia	..	1·47	..	..	..	..	0·37
Potash	..	..	..	..	..	..	0·83
Soda	..	..	..	4·77	..	..	0·59
Chlorine	traces	traces	trace	trace	traces	traces	trace
Phosphoric acid			1·00	0·32	0·95	0·90	trace
Sulphuric acid			trace	trace	0·28	trace	..
	95·29	98·77	100·38	100·46	98·71	100·58	100·99

Analysis of iron ore from Port Madoc, South Wales.

.....	5·10
.....	1·14
.....	17·56
.....	15·06
.....	12·73
.....	20·32
Peroxide of iron	23·40
Peroxide of manganese	4·27
Nickel and cobalt oxides	0·41
.....	1·18
.....	0·39
.....	trace
.....	trace
	101·56

Analyses of Ten Specimens of Cast Iron, made from South Staffordshire Iron Ore, chiefly West of Dudley.

Iron from Cold Blast.

	I.	III.	IV.	V.
Iron	94·10	96·57	94·53	94·42
Combined carbon (*a*)	1·87	0·95	c.	c.
Uncombined carbon (*b*)	1·92	1·67	1·98 3·71*	2·73 4·05
Silica	1·30	0·51		
Manganese	1·12	1·16	0·33	0·94
Cobalt	trace	..	..	trace
Chromium	trace			
Calcium	0·05	trace	0·25	0·16
Sodium	0·16	trace	0·30	0·34
Potassium	trace	0·42		
Sulphur	trace	0·11	0·05	trace
Phosphorus	0·21	0·36	0·03	0·36
	100·73	101·75	99·20	100·27

Iron from Hot Blast.

							VII.	VIII.
Iron	89·53	92·98	93·84	92·90			95·23	95·80
Carbon	c.	c.	c.	c.			C (*a*) 1·77	2·72
Carbon	3·27 7·93	3·11 6·51	2·98 5·54	0·87 6·83			C (*b*) 0·49	0·26
Silica, &c.							0·31	0·11
Manganese	1·71	1·30	0·72	0·62			0·34	0·54
Calcium	0·11	trace	0·34	0·06			0·10	0·06
Sodium	0·41	0·37	0·39	0·30			0·19	0·14
Potassium	..	..	trace	trace				
Sulphur	0·07	trace	minute trace	trace			trace	trace
Phosphorus	0·54	lost	0·07	0·40			0·12	0·37
	100·30	101·16	100·90	101·11			98·55	100·00

* The figures 3·71 in No. IV. (cold blast), as well as the corresponding figures in No. V. (cold blast), and Nos. I., III., IV. and V. (hot blast), indicate the per-centage of substance separated and weighed on filter, consisting, with the exception of No. V. (hot blast), principally of carbon and small quantities of silica, oxide of iron, lime, &c., and which I regret time did not permit me to make an accurate quantitative examination of. The figures on the left, marked C., indicate the *entire* amount of carbon in the iron.

The white iron can, on the other hand, be brought to assume the aspect and fracture of the gray iron by being frequently heated to whiteness and very gradually cooled down. It would seem, in fact, as though the carbon, in part at least, were held in solution in the molten iron, just as certain salts are in hot water; and that in the gray iron, during the process of cooling, a considerable part had been deposited in an uncombined state, either from its being present in larger quantity or from being more slowly cooled.

Difference in the per-centage of Phosphorus in the Hot and Cold Blast Iron.

	I.*	II.	III.	IV.	V.	VI.	VII.	VIII.
Cold blast....	0·47	0·41	0·31	0·20	0·21	0·36	0·03	0·36
Hot blast	0·51	0·55	0·50	0·71	0·54	..	0·07	0·40

On the Composition of the Titanium Crystals which are met with in the Slags of the Blast Furnaces. By Prof. Wöhler.

It had hitherto been believed that the cubic crystals of titanium, which occur pretty frequently in the slags of the blast furnaces, were metallic titanium; I have just discovered that these cubes are formed of cyanuret and of nitruret of titanium. They contain 18 per cent. of nitrogen and 4 per cent. of carbon, and are represented by the formula $Ti\,C^2N + 3Ti^3\,N$ or $(TiCy + 3Ti^3\,N)$. I have likewise found that the titanium obtained by the method of Prof. H. Rose is a nitruret of titanium containing 28 per cent. of nitrogen, and with the formula $Ti^3\,N^2$.

The cubic crystals, fused with hydrate of potash, furnish ammoniacal gas. The same crystals, heated in a current of chlorine, yield a liquid chloride of titanium and a very volatile crystalline substance, which is a combination of cyanide and of chloride of titanium. This latter substance may be obtained directly by placing chloride of titanium in contact with some gaseous chloride of cyanogen. The gas is absorbed without disengagement of heat.

By heating the cubes to redness in a current of steam, the latter is decomposed and hydrogen obtained, as had been previously announced by M. Regnault; but there is moreover produced some ammonia and some hydrocyanic acid. The titanic acid which remains exhibits the same octahedral form as anatase; it is artificial anatase.

I have succeeded in forming the cubic crystals by heating in the forge-furnace a mixture of titanic acid and ferrocyanide of potassium. With respect to the simple nitruret, it is very easily obtained by heating to redness titanic acid in a current of gaseous ammonia, cyanogen or hydrocyanic acid. This substance always occurs with a remarkable metallic lustre.

I have been able by the same process to obtain the nitrurets of several other metals, which I am at present engaged in examining. —*Comptes Rendus*, Nov. 5, 1849.

* The first four numbers are taken from the former series before named; those from V. to VIII. from the present series. They are not numbered as in the Table of Analyses, but it will easily be seen to which they refer.

Natural Sources and new Mode of preparing Sulphuric Acid. *By* C. Blondeau.

Abundant sources of sulphuric acid exist in nature. M. Boussingault has described several acid waters in America, and particularly the Rio-Vinagre or Pasiambo, of which 1000 parts contain 2 parts of sulphuric acid. According to M. Boussingault's estimate, the Pasiambo supplies 38610 kilogrammes of sulphuric acid in 24 hours, and this quantity is much exceeded by the discovery made in the Paramo de Riuz by M. Degenhart, the water there containing, according to M. Lewy's analysis, three times as much sulphuric acid as the Pasiambo. Whence come these enormous quantities of the acid? what are the processes which nature employs in their formation? The author states, that a phænomenon which he observed in the department of Aveyron gave him an opportunity of describing the natural formation of an acid so much employed in the arts, and which placed him in a condition, in the localities which he has examined, of readily manufacturing sulphuric acid, without having recourse to the complicated processes generally employed.

In the coal-measures of Aveyron, and particularly in the environs of Cransac (arrondissement de Villefranche), spontaneous combustion of the soil is observed to occur, which is evidenced by the disengagement of gas and vapours, which at a distance resemble a small volcano. On approaching the place where this combustion occurs, it is evident that the earth has been mined, and large crevices are discovered from time to time, from which are emitted much aqueous vapour and acid fumes. At the edges of these fissures the heat becomes intolerable, and surprise ceases to be excited that the effects of this heat, combined with the action of acid gases, should have modified so completely the places in which these chemical actions occur.

In some spots of the burning mountain, there occur enormous rocks formed of conglomerates, which, having undergone the action of fire, are completely changed in appearance, and are united by a cement, which owing to the action of heat has a brick-red colour.

The surface of the burning mountain consisted of grits, schists and argills; these substances have assumed the appearance of chalcedonies, jaspers, enamels, glass and bricks, and sometimes even the cavernous appearance of volcanic stones. The aggregations which these substances have formed with the clay have in some cases acquired the hardness of the most compact stones. The soil, gradually mined by the chemical agency occurring within it, eventually sinks, occasioning the formation of basins, which, by their conical form, resemble in some degree the craters of volcanos; it is through these vents that columns of vapour are disengaged, which sometimes rise to a great height in the air, and are at other times dispersed by the wind in the valleys.

In these places a number of saline concretions, efflorescences, crystals of sulphur and hydrochlorate of ammonia are met with; these products have been converted to useful purposes, and dissolved in

rain-water: they constitute the mineral waters frequently employed in the locality now described.

The causes of the phænomena become evident to any one who has ascertained the presence of sulphuret of iron, which occurs abundantly in the various strata of coal country which constitute this locality.

This sulphuret, in contact with water and with atmospheric air, burns and gives rise to sulphurous acid gas, which is converted into sulphuric acid by the influence of air and of bases, such as alumina and oxide of iron. The sulphates of iron and alumina which form under these circumstances are decomposed by the action of heat, and sulphuric acid is set free.

The temperature resulting from these different reactions is sometimes sufficiently high to occasion the combustion of the coal-beds which are near the surface, and the products of the combustion of the coal are added to the vapour of water and of sulphuric acid, and thus increase the grandeur of the phænomenon. The sulphuric acid which arises under the conditions described, exerts a very energetic action on the mineral and organic substances which it meets with in its passage; the trunks of the trees which occur in the neighbourhood of the burning mountain are covered with the black colour of substances which have been immersed in sulphuric acid. Mineral substances are also strongly acted upon by this powerful acid, which simultaneously attacks silica, alumina, lime, oxide of iron, the earths and alkalies which enter into the composition of rocks, and eventually sulphates are produced, among which is the double sulphate of potash and alumina (alum) in sufficient quantity to be useful.

The author analysed the efflorescences collected on the burning mountain of Cransac. These efflorescences were white, strongly acid, reddened tincture of litmus, and attracted moisture from the air. After drying *in vacuo* by the air-pump, 50 grammes were dissolved in a litre of distilled water, and the solution was treated as if it had been a common mineral water.

The results of the analyses were:—

Sulphate of potash and alumina . .	24·25
Sulphate of alumina	53·31
Sulphate of magnesia	3·47
Sulphate of manganese	1·35
Sulphate of iron	10·29
Free sulphuric acid	7·33
	100·00

On examining the natural process which gives rise to the large quantities of sulphuric acid, occurring not only combined with bases, but also uncombined, it occurred to M. Blondeau to examine whether under similar conditions sulphuric acid might not be immediately produced from sulphurous acid gas.

For this purpose some argillaceous sand was put into a porcelain tube, one of the ends of which communicated with two vessels, from one of which sulphurous acid, and from the other vapour of water

was disengaged, and at the same time air was passed into the interior of the apparatus by means of a gasometer. At the other end of the porcelain tube a bent tube was adopted, which was immersed in water in a two-necked bottle, to one of which was fixed a disengaging tube. The apparatus thus arranged, the porcelain tube was surrounded with burning charcoal, so as to heat it to dull redness, and the sulphurous acid gas, air and the vapour of water were slowly passed into it. The substance disengaged at the end of the tube was sulphuric acid; taking care to supply an excess of air, but very little sulphurous acid is disengaged, the whole of it being converted into sulphuric acid.

To go from this laboratory experiment to a manufacturing one, sulphurous acid must be produced by the combustion of sulphur or sulphurets, and the products of the combustion passed into a cylinder of cast-iron strongly heated and containing argillaceous sand, passing into it at the same time excess of the vapour of water. The sulphuric acid will be received at the other end of the cylinder. The author is of opinion that no doubt can be entertained of the superiority of this plan to that which is at present adopted, and that by employing an apparatus thus constructed, sulphuric acid will be procured at a lower price than is at present the case.—*Comptes Rendus*, Oct. 15, 1849; and *Philosophical Magazine* for December.

On the Action of Nitric Acid on Woody Fibre.

TO THE EDITOR OF THE CHEMICAL GAZETTE.

Sir,—The last Number of your Journal contains a summary of Mr. Porter's research on one of the products of oxidation of woody fibre. As it will be found that these artificial processes afford us an important, and in many cases the only clue we can obtain to a right understanding of natural phænomena in connexion with vegetable physiology, the following remarks may not be considered irrelevant.

It appears that M. Sacc had previously made a research so nearly allied to the one alluded to, that under ordinary circumstances we should have expected a greater conformity in analytical results; by adopting, however, Mr. Porter's formula, we at once obtain a relative view of the composition of the two bodies in question. Thus, taking hydrogen as unity—

	Equivs.		Per cent.
Carbon.....	16 =	96	41·92
Hydrogen	13	13	5·67
Oxygen	15	120	52·41
		229	100·00

which, considering the discrepancies in the analyses, is a tolerable approximation.

Now $C^{16} H^{13} O^{15} = C^{16} H^{12} O^{14} + HO$, or the body obtained by Mr. Porter plus 1 equiv. of water.

By adopting another empirical formula, the alliance between the body obtained by M. Sacc and lignine may be readily traced; thus

$$C^{12} H^{10} O^{11} = C^{12} H^{8} O^{8} + 2HO + O$$
$$= \text{lignine} + 2HO + O.$$

Of course this mode of reasoning is only adapted to the purpose of tracing analogies in a general manner; but having lately been engaged in the study of the changes which take place in the bulb of the *Ruta baga* in different stages of development, I am interested to observe how nearly the processes conducted in the laboratory and in nature resemble each other, both being a continuous process of oxidation.

The formula for pectic acid advanced by M. Fremy may probably be advantageously altered for $C^{16} H^{12} O^{15}$; in which case it becomes the body obtained by Mr. Porter plus 1 equiv. of oxygen.

I remain, Sir,

Douglas, Isle of Man,
Dec. 8th, 1849.

Your obedient Servant,
Geo. Kemp, M.D. Cantab.

On the Salts of Perchloric and Periodic Acids with Organic Bases. *By* J. Bœdeker.

The acids employed for the preparation of these salts were prepared according to the usual methods, and were pure and perfectly free from sulphuric acid.

Perchlorate of Cinchonine was obtained by decomposing a solution of sulphate of cinchonine accurately with one of perchlorate of baryta. The solution could be evaporated to crystallization without the least decomposition. The salt forms very large, permanent, rhomboidal prisms, and is characterized by a strong lustre and a beautiful dichroism of blue and yellow, which even its dilute solution exhibits. It is readily soluble in water and alcohol. At 320° it melts and loses its water of crystallization; at a higher temperature it explodes with a considerable flame.

The salt dried at 86° lost at 320° 3·57 per cent. of water. In order to determine the amount of chlorine, the salt was mixed with 4 times its weight of carbonate of soda, heated to redness, and the chlorine precipitated by solution of silver; it is evident therefore that the salt is neutral perchlorate of cinchonine with 1 atom water of crystallization. The result agrees best with the formula $C^{19} H^{11} NO$, recently adopted by Laurent for cinchonine:—

	Found.	Calculated.
Perchloric acid	35·41	35·63
Cinchonine with 1HO	60·51	60·87
Water.....	3·57	3·50

In an attempt to precipitate the perchloric acid from an alcoholic solution of the salt by an alcoholic solution of acetate of potash as perchlorate of potash, a third of the perchloric acid remained with the cinchonine unprecipitated.

Perchlorate of Quinine was also obtained by the decomposition of a solution of the sulphate with perchlorate of baryta. When

the solution filtered from the sulphate of baryta was concentrated by evaporation, the salt separated on cooling in heavy yellowish oily drops, which with the gentlest heat dissolved again entirely; the salt then separated on cooling in crystals. The mother-liquor, on further evaporation, furnished the oily modification of the salt, which however immediately solidified into an aggregation of crystals as soon as a solid crystal was placed in contact with it. This quinine salt forms striated irregular prisms, which exhibit a faint dichroism of blue and yellow. The solution, especially that in alcohol, presents the most beautiful dichroism. It melts at the ordinary temperature, under a bell-glass over sulphuric acid, to a clear brittle mass, with a very beautiful dichroism of blue and yellow. Heated with water, it melts to a clear liquid, which gradually dissolves in the water; the crystals behave in the same manner. It dissolves readily in alcohol. At 113° the crystals began to melt, and up to 230° lost 14·3 per cent. of water; at 302° the mass puffed up considerably, became solid again at 320°, and had lost 18·63 per cent. of water. At a higher temperature it explodes violently and with considerable flame. Analysed in the same manner as the cinchonine salt, it proved to be neutral perchlorate of quinine, $C^{19}H^{11}NO^2$ +7aq, 5 atoms of which it loses at about 212°:—

	Found.	Calculated.
Perchloric acid	28·21	28·71
Quinine with 1HO	50·63	51·53
Water.....	18·63	19·76

With a certain concentration of the solution of the salt, it no longer separates in an oily form, but in crystals with a different amount of water, only 2 atoms. This salt forms rhombic prisms which possess considerable lustre, and the same dichroism as the first, but in a still higher degree, both in the solid and dissolved state. It likewise dissolves at a gentle heat under water to an oil, but alone not before 410°, when it loses 6·5 per cent. of water. 2 atoms require 6·31.

Perchloride of Strychnine.—By decomposing boiling solutions of sulphate of strychnine and perchlorate of baryta, this salt immediately separates on cooling in crystals. It forms small vitreous rhombic prisms of a pale yellow colour, which is probably not essential. It is sparingly soluble in cold water, but dissolves in alcohol. When heated, the crystals lose water, and become opake, and explode when heated more strongly. The salt, dried at 86° and gradually heated to 338°, lost 3·8 per cent. of water. The estimation of the chlorine showed that it was the neutral perchlorate of strychnine with 2 atoms of water of crystallization:—

	Found.	Calculated.
Perchloric acid	19·21	19·58
Strychnine with 1HO	76·99	76·56
Water.....	3·80	3·86

Perchlorate of Brucine is obtained by saturating dilute perchloric acid with pure brucine; it forms palish yellow prisms of considerable lustre, very sparingly soluble in cold water and alcohol, more readily soluble in hot, but far less so than the salt of strych-

nine. Heated up to 338°, it lost 5·4 per cent. of water; at a higher temperature it explodes.

Perchlorate of Morphine was obtained by saturating pure morphine with an aqueous solution of perchloric acid. It forms white, silky, fasciculate, acicular crystals, tolerably soluble in water and alcohol, melts at 302°, losing 8·34 per cent. water, and explodes at a higher temperature. According to analysis, it is a neutral salt, with 4 atoms of water of crystallization:—

	Found.	Calculated.
Perchloric acid	21·08	21·32
Morphine with 1HO.....	70·58	70·29
Water.....	8·34	8·39

Perchlorate of Codeine, prepared like the preceding, forms very similar silky fasciculate needles, but is far more soluble in alcohol and water than that. It explodes.

Perchlorate of Furfurine, prepared by dissolving furfurine in very dilute hot perchloric acid. It forms very long, slender, glassy, brittle prisms; has a disagreeable, saline, bitter taste, and is readily soluble in alcohol and water. At 140° the crystals become opake, and fall to a powder; between 302° and 320° they melt to a clear mass, which is brittle when cold; at a higher temperature it explodes. It is the neutral salt with 2 atoms of water of crystallization:—

	Found.	Calculated.
Perchloric acid	23·69	23·64
Furfurine with 1HO	72·26	71·71
Water.....	4·04	4·65

I did not succeed in preparing the perchlorates of atropine, solanine, veratrine, pelosine, nicotine, caffeine, piperine, urea, rhodaline and thialdine. Nicotine and thialdine were instantly destroyed by the perchloric acid. The other bases dissolved readily in the acid, but crystallized from it unaltered on spontaneous evaporation—the rhodaline and caffeine in extremely beautiful crystals.

Periodate of Strychnine was obtained by dissolving strychnine in very dilute hot periodic acid; it forms colourless rectangular prisms of considerable lustre, and is pretty readily soluble in hot water and alcohol. The crystals become opake over sulphuric acid. When heated, they explode with flame and a dense vapour. When the solution is evaporated in the air, it becomes brown, the salt being decomposed.

Periodate of Brucine is very similar to the preceding, but of a yellow colour; it is pretty soluble in hot water and alcohol, but is readily altered in solution by exposure to the air. When heated, it explodes.

Morphine, quinine, cinchonine and furfurine could not be combined directly with periodic acid, the acid and base being mutually decomposed with separation of iodine. This decomposition took place very rapidly with morphine.

All attempts to obtain salts of organic bases with permanganic acid proved fruitless, owing to the ready decomposability of the acid.—Liebig's *Annalen*, July 1849.

On the Dry Distillation of the Camphorate of Lime.
By C. Gerhardt *and* Lies-Bodart.

The dry distillation of the lime salts of organic acids furnishes interesting products, serving as transitions between the different series. With the exception of suberic acid, only monobasic acids have been examined in this respect; our experiments have been made with camphoric acid, the characters of which as a bibasic acid are well marked. We have found that camphorate of lime gives by heat an essential oil, possessing the odour of peppermint, and in composition similar to that of the acetonides of the monobasic acids. This oil contains $C^9H^{14}O^*=2$ vols. vapour. It is remarkable by the metamorphosis which it experiences with anhydrous phosphoric acid, which agent converts it into cumene $=C^9H^{12}=2$ vols. of vapour, the identity of which we have ascertained by analysis, and by the easy formation of sulphocumerate of baryta, $C^9H^{11}BaSO^3$. This reaction connects the camphoric series with the cumenic, and consequently with the benzoic series. As camphoric acid, although bibasic, does not form an exception to the general rule, it is possible that the anomaly presented by suberic acid will be removed by new and more complete researches.—*Comptes Rendus*, Nov. 5, 1849.

PROCEEDINGS OF SOCIETIES.

Chemical Society of London.

Nov. 5, 1849. (The President, Mr. Richard Phillips, in the Chair.) The following papers were read:—

"On a new Series of Organic Bodies containing Metals and Phosphorus," by E. Frankland, Ph.D.

In continuing his researches on the isolation of the organic radicals, and more particularly the action of zinc on the iodide of ethyle, Dr. Frankland finds that when the white crystalline residue, left in the decomposition-tube by the action of zinc on the iodide of methyle, is submitted to distillation, it yields a colourless pellucid liquid of a peculiarly penetrating and nauseous odour, which inflames spontaneously on contact with atmospheric air or oxygen, forming dense clouds of oxide of zinc. The vapour is highly poisonous; it decomposes water with as much violence as potassium. It is composed of 1 equiv. of methyle and 1 equiv. of zinc. The corresponding compound of ethyle and zinc is also described. It is highly probable that the decomposition of these iodides by arsenic and tin will generate compound radicals analogous to cacodyle. The iodide of methyle would probably yield cacodyle itself. When phosphorus is employed instead of a metal, decomposition readily ensues; and as no gases are evolved, the author considers that a series of bases analogous to that of Paul Thenard may result. The existence of hydrogen compounds—of arsenic, antimony and tellurium, and the

* Gerhardt's equivalents.

substitution of ethyle and methyle for hydrogen in the new bases of Wurtz—point out the striking similarity between the respective functions of these radicals and that element, and seem to warrant the expectation that compounds of zinc, arsenic, antimony and phosphorus with ethyle, methyle, butyryle, valyle, amyle and phenyle may be obtained. Some of these are already known. The author has made several preliminary experiments, which seem to promise success, the results of which will be shortly laid before the Society. Dr. Hofmann exhibited a specimen of the zinc-methyle he had obtained from Dr. Frankland, and demonstrated its spontaneous inflammability.

"Researches on the Volatile Organic Bases," by Dr. Hofmann. "Action of Acids and Bases upon Cyaniline."

In order to verify the composition of cyaniline, which is formed in a very unusual manner, namely, by the direct combination of aniline with cyanogen without elimination of hydrogen, the author has studied the actions of acids and bases upon this compound. By the actions of dilute hydrochloric acid, cyaniline yields five different products,—chloride of ammonium, hydrochlorate of aniline, oxanilide, oxamide, and oxamide-oxanilide. The formation of derivatives of oxalic acid proves that the cyanogen must be in direct combination with the aniline; had it been in the form of hydrocyanic acid, derivatives of formic acid would have been produced. Again, had cyaniline been formed by a process of substitution, the product of decomposition would have belonged to the carbonic acid series. By fusion with potash, cyaniline is converted into aniline, ammonia and carbonic acid, hydrogen being evolved. This decomposition agrees equally well with the formula originally proposed.

"Metamorphosis of Dicyanomelaniline, formations of the Aniline Term corresponding to Cyanic Acid," by Dr. Hofmann.

Dicyanomelaniline, the base produced by the action of cyanogen upon melaniline, is likewise rapidly decomposed by acids. The product of the reaction is an indifferent crystalline body, which may be considered as binoxalate of melaniline —4 equivs. of water. This substance regenerates oxalic acid and melaniline by the action of acids or bases. When subjected to dry distillation, it gives rise to the formation of a remarkable liquid, distinguished by a most powerful odour, which is the cyanic acid of the aniline series. In this compound the original character of cyanic acid is retained; with acids, bases or water it yields the various products of the ordinary cyanic acid, containing however invariably the elementary difference $C^{12}H^{4}$, distinguishing aniline from ammonia. Dr. Hofmann then discusses the process by which anilocyanic acid is formed in the dry distillation of melanoxamide; and in conclusion calls attention to the great analogy presented by the aniline series with those of the bases derived from methyle and ethyle, discovered by M. Wurtz, the common type of both being ammonia.

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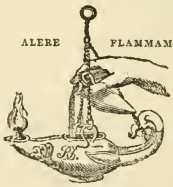

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